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# Environmental Implications of Changes in the Brominated Chemicals Industry

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In light of the large-scale changes occuring within the bromine-based chemicals industry, the U.S. Environmental Protection Agency commissioned a study to investigate the potential for adverse environmental effects that might result from such changes. In particular, EPA was interested in learning if the existing excess capacity to produce bromine and ethylene dibromide has or would stimulate the industry to seek alternative uses for bromine that could result in new environmental concerns. To accomplish the objectives of the study, an extensive literature review was conducted, followed by personal contacts with knowledgeable individuals and by independent analysis. Our efforts were concentrated on present and future markets, exposure potential, and risk assessment.

The study indicates, in general, the environmental effects resulting from changes in the industry are relatively minor or that the potential problems have already been recognized and are being addressed by EPA. However, several areas do require further attention: the brominated flame retardants industry; the effect of methyl bromide on stratospheric ozone; the lack of carcinogenicity and food-residue data for methyl bromide; the environmental effects of bromine chloride utilization; chemicals used for petroleum production; vinyl bromide risk assessment; and thallium bromide optical fibers.

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# ENVIRONMENTAL IMPLICATIONS OF CHANGES IN THE BROMINATED CHEMICALS INDUSTRY

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# ABSTRACT

In light of the large-scale changes occurring within the bromine-based chemicals industry, the U.S. Environmental Protection Agency commissioned a study to investigate the potential for adverse environmental effects that might result from such changes. In particular, EPA was interested in learning if the existing excess capacity to produce bromine and ethylene dibromide has or would stimulate the industry to seek alternate uses for bromine that could result in new environmental concerns.

To accomplish the objectives of the study, an extensive literature review was conducted, followed by personal contacts with knowledgeable individuals and by independent analysis. Our efforts were concentrated on present and future markets, exposure potential, and risk assessment.

The greatest potential environmental hazard may not be with emissions of bromine itself, but rather with low-level or accidental exposure to specific brominated chemicals that are potentially carcinogenic or teratogenic. Ethylene dibromide, "tris," and vinyl bromide have been shown to cause cancer in test animals.

Many gaps exist in the information available on the bromine-based chemicals industry. Where necessary, we made assumptions allowing us to temporarily bridge the gaps. In most cases, our analyses indicate that filling the data gaps should not be a high priority in light of other pressing issues that EPA faces. We feel that, in general, the environmental effects are relatively minor or that the problems are already recognized and are being addressed by EPA. However, several areas do require further attention: the brominated flame retardants industry; the effect of methyl bromide on stratospheric ozone; the lack of carcinogenicity and food-residue data for methyl bromide; the environmental effects of bromine chloride utilization; chemicals used for petroleum production; vinyl bromide risk assessment; and thallium bromide optical fibers.

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# List of Abbreviations and Symbols

| | |
|---|---|
| day | d |
| foot (feet) | ft |
| gallon(s) | gal |
| gram | g |
| hour(s) | hr |
| inch(es) | in |
| kilogram(s) | kg |
| kilometer(s) | km |
| liter(s) | l |
| meter(s) | m |
| microgram | µg |
| million gallons per day | mgd |
| minute(s) | min |
| nanogram(s) | ng |
| nanometer(s) | nm |
| parts per billion | ppb |
| parts per million | ppm |
| parts per trillion | ppt |
| percent | % |
| pound(s) | lb |
| second(s) | s |
| U.S. Environmental Protection Agency | EPA |
| yard(s) | yd |
| year(s) | yr |

# 1.0 INTRODUCTION

## 1.1 Background, Scope, and Methodology

Because of changing market conditions, much of which is attributable to various environmental considerations, substantial alterations in existing production and consumption patterns of bromine compounds have occurred. At the outset of the study, Winzler and Kelly was aware that several factors were acting to reduce the level of bromine compound demand:

- Lead phase-down. EPA's phase-down of the lead content of gasoline has already resulted in substantial reductions in lead use (and hence ethylene dibromide use) in gasoline.

- DBCP ban. EPA suspended nearly all uses of the pesticide dibromochloropropane on 29 October 1979. Future use of DBCP appears to be very limited, if not nil. DBCP is also controlled by OSHA.

- Ethylene dibromide regulation. Ethylene dibromide is under consideration by EPA for regulation under Section 112 of the Clear Air Act (NESHAP). Such regulation would result in an emission standard for ethylene dibromide, or, where this is infeasible, design, equipment, work practice, or operational standards may be imposed. The effect of such regulations on ethylene dibromide consumption is unclear. Vinyl chloride is under NESHAP regulation, and its domestic production and consumption remains very high.

- Tris ban. Tris(2,3-dibromopropyl)phosphate, a flame-retardant used in textiles, is no longer used for this purpose because of its carcinogenicity and exposure potential.

- PBB contamination. The contamination of animal feed with polybrominated biphenyls (a group of fire retardants) in 1973 in Michigan heightened the public's awareness of this group of chemicals, and their use has nearly stopped since then.

- Ethylene dibromide replacement in some fumigation. The technology for using gamma radiaton for fruit fumigation has been developed, and this could replace ethylene dibromide for this purpose.

However, we were also aware of other market factors increasing the demand for bromines:

- Greater use of BrCl for water disinfection. The trend toward reducing the residual chlorine demand in effluents appears to be resulting in a strong demand for bromine chloride.

- Calcium bromide use in drilling fluid. The use of calcium bromide in well-drilling fluid is expanding very rapidly.
- Fire retardants. The use of brominated compounds as fire retardants represents a strong market.
- Ethylene dibromide as fumigant. The use of ethylene dibromide as an agricultural crop and seed fumigant is increasing.
- Flame retardant not found to be carcinogenic. No carcinogenic response was observed in rats exposed to dibromoneopentyl/glycol, a reactive flame retardant widely used in unsaturated polyester resins and polyurethane foam.

The very dynamic nature of the bromine market is of interest to EPA because of the potential for new or expanded uses for bromine, which in turn might result in environmental problems from specific compounds. The objective of the proposed study was to evaluate this potential and to assess the implications for EPA's regulatory mission.

The approach to achieving the objectives of the study included the following major elements where desirable and practical:

- Identification of significant bromine compounds, their producers and users, and the quantities involved.
- Identification of future trends in production and use.
- Estimation of emission rates.
- Characterization of environmental fate of bromine compounds, including estimates of ambient concentrations.
- Review of pertinent toxicological data, with emphasis on carcinogenicity and teratogenicity.
- Identification of pollution-control technologies and analytical methods.
- Rough assessment of carcinogenic and non-carcinogenic risk.
- Evaluation of likelihood and magnitude of potential problems and the likely regulatory pathway and control strategies.

The study progressed by first conducting a literature review based upon an extensive computerized bibliographic search. The literature review was followed by a campaign of personal contacts by telephone with individuals working in industry, governments, and academe, the purpose of which was to clarify the literature and to fill some of the major information gaps in the literature. Then, we proceeded to complete the tasks mentioned above, making independent assumptions and calculations where needed, the most important compounds receiving the greatest attention.

## 1.2 Summary of Results

The major uses for bromine in the U.S. are for manufacturing ethylene dibromide, flame retardants, calcium bromide, methyl bromide, and bromine chloride. Despite the declining usage of ethylene dibromide (EDB) in gasoline, EDB is still responsible for nearly half of the total domestic bromine demand. At least 76 brominated organic chemicals were listed by the U.S. International Trade Commission as being produced commercially during 1978.

The salient features of the 1979 domestic bromine industry according to the U.S. Bureau of Mines were:

- The U.S. produced 65 percent of the world's bromine.
- U.S. exports were far greater than imports.
- Nearly half of the U.S. demand for bromine was supplied as the gasoline additive ethylene dibromide (48 percent), followed by fire retardants (29 percent), sanitation preparations (16 percent), and other uses (6 percent).

Several significant changes have occurred in the bromine industry over the last several years, the most important of which has been the decline in ethylene dibromide utilization as a gasoline additive.

Since the U.S. Environmental Protection Agency's gasoline lead phase-down program began in 1973, and its ban against the use of leaded gasoline in automobiles equipped with catalytic converters began some time later, ethylene dibromide's use as a combustion-exhaust lead scavenger has declined substantially -- roughly 25% between 1974 and 1979 -- resulting in 60 x $10^6$ lb less bromine being used for EDB production in 1979 than in 1974. This situation, plus the addition of 200 x $10^6$ lb bromine production capacity (nameplate) during 1975 and 1976, left the bromine industry with a large excess production capacity for ethylene dibromide and bromine. No other sizeable products exist for which the excess EDB capacity can be used.

Bromine-based fire-retardant chemicals have shown a moderately strong and steady increase in demand over the years. However, great uncertainty exists regarding the actual rates of production and consumption. Because of the increasing demand for fire retardants, the virtual elimination of the production and use of the brominated flame retardants "tris" and polybrominated biphenyls in the U.S. during the 1970's did not cause a dip in the overall demand for fire retardants.

The demand for calcium bromide has grown tremendously since its introduction as a well-drilling fluid in 1972. Since 1976, domestic production increased from nearly zero to over 100 x $10^6$ lb (42% bromine content) in 1978. This increased demand stems from the oil and gas industry's efforts to increase production.

"Sanitation preparations," a group designation of the Bureau of Mines that includes bromine chloride and elemental bromine used as water disinfectants and methyl bromide and ethylene dibromide used as fumigants, experienced a diminishing demand until 1979, when domestic demand increased 73 percent over the 1978 level. Virtually all of the "sanitary preparations" group can be accounted for by the fumigants methyl bromide and ethylene dibromide through 1978. In 1979, a new facility with a production capacity for bromine chloride of 30 x $10^6$ lb/yr (21 x $10^6$ lb bromine per yr) began operating, helping to account for the large increase in demand.

The historical data show a gradual increase in production and demand for bromine; a widening in the difference between production and demand, indicating increased exports in the 1970's; a moderately high increase in the demand for fire retardants and a decrease for EDB; and sharp increases in production capacity during 1975 and 1976.

A crude forecast of EDB demand between 1973 and 1979, assuming that leaded gasoline consumption had not been diminished by EPA regulations, indicated that there would likely have been only a small excess bromine production capacity by 1979, rather than the large excess that exists now.

Domestic bromine demand is expected to increase at a rate of 2 to 5 percent annually (compounded annually) to 1985, driven by demand increases for flame retardants (4 to 8%/yr), bromine chloride (15%/yr), calcium bromide (15%/yr), and methyl bromide (4 to 5%/yr). Demand for ethylene dibromide will continue declining, perhaps at a rate of 15 percent per year. The overall demand for bromine will depend heavily on the demand for calcium bromide.

Forecasts to the year 2000 indicate a low overall growth rate for bromine of 1.4%/yr. However, demand growth for "sanitation preparations," fire retardants, and calcium bromide drilling fluids are expected to be substantially greater. Table 1.2-1 summarizes the near- and long-range forecasts for bromine.

While bromine production in the U.S. has increased modestly over the years, production in Israel has more than doubled since 1976, although U.S. production was still five-fold greater than Israel's in 1979. Moreover, in an effort to boost exports, Israel plans on doubling its bromine production from 53,000 tonnes (116 x $10^6$ lb) in 1980 to 100,000 tonnes (220 x $10^6$ lb) per year by 1984.

Imports increased greatly during 1978 and 1979, although they are still only 1% or less of domestic consumption. During 1979, approximately 99% of the accounted-for imports were from Israel.

Table 1.2-1. Forecasts of Bromine Demand by End Use to Year 2000[a]
(Million Pounds)

|  |  |  | 2000 Contingency forecast for United States |  |  |  |
|---|---|---|---|---|---|---|
|  |  |  | Forecast range |  | Probable |  |
| End Use | 1978 | 1985 Contingency Forecast[b] | Low | High |  | (% Annual Growth)[e] |
| Petroleum | 220.5 | 80 | 10 | 150 | 75 | -4.8 |
| Sanitary preparations | 35.8 | 88[c] | 65 | 150 | 100 | 4.8 |
| Fire retardants | 70.0 | 166 | 50 | 150 | 150 | 3.5 |
| Other | 49.5 | 123[d] | 30 | 200 | 175 | 5.9 |
| Total | 375.8 | 457 | 155 | 650 | 500 | 1.3 |

---

[a] Source: Lyday, 1980a, unless noted otherwise.

[b] Source: Winzler and Kelly forecast, Section 2.1.1.

[c] "Sanitary preparations" includes methyl bromide and bromine chloride.

[d] "Other" uses includes calcium bromide and elemental bromine.

[e] Compounded annual rate for the 22-year period 1979 through 2000, calculated by Winzler and Kelly.

Exports increased significantly over 1977, although declining 6% from 1978 to 1979. Exports represented approximately 18 percent of the bromine produced in the U.S. during 1979. Israel is aggressively pursuing a program of increased production of bromine and bromine-based chemicals for foreign markets. Because bromine in its lead-lined shipping containers is heavy, and therefore costly to transport, Israel will likely be able to capture a portion of U.S. exports to areas that are closer to Israel than to the U.S. Nevertheless, U.S. producers feel that their foreign markets will remain strong. The strength of the recent export market is thought to be due to the approval of a lightweight container for shipping bromine. Also, to increase profits and safety, producers tend to ship bromine derivatives rather than bromine itself, according to a major producer.

The greatest potential environmental hazard may not be with emissions of bromine itself, but rather with low-level or accidental exposure to specific brominated chemicals that are potentially carcinogenic or teratogenic. Ethylene dibromide, "tris," and vinyl bromide have been shown to cause cancer in test animals.

Many gaps exist in the information available on the bromine-based chemicals industry. Where necessary, we made assumptions allowing us to at least tentatively bridge the gaps. In most cases, our analyses indicate that filling the data gaps should not be a high priority in light of other pressing issues that EPA faces. That is, in general, we feel that the environmental effects are relatively minor or that the problems are already recognized and are being addressed by EPA. However, several issues do require further attention:

- Better definition of the brominated flame retardants industry and associated environmental effects is needed. A current EPA-sponsored study strives to achieve this goal.

- The effect of methyl bromide on stratospheric ozone deserves greater attention.

- Studies of carcinogenicity and the gathering of food-residue data for methyl bromide would be useful for EPA's planned review under the Federal Insecticide, Fungicide, and Rodenticide Act.

- Additional research into the environmental effects of bromine chloride utilization would be useful to further substantiate the evidence that bromochlorination is less environmentally damaging than chlorination.

- Better characterization of potential environmental effects of calcium bromide drilling fluid and DTAB, a brominated surfactant used in tertiary oil recovery, may be warranted. Considering that drilling activities have expanded substantially in recent years, a review of current petroleum drilling and production technologies would be useful and timely.

- Because vinyl bromide is carcinogenic in test animals, a detailed risk assessment would be appropriate.
- Further market and environmental assessment for thallium bromide optical fibers would be appropriate exploratory research.
- Further market and environmental assessment for bromosilanes may be advisable (Section 2.22).

# 2.0 MARKET AND ENVIRONMENTAL ASSESSMENT OF THE BROMINE INDUSTRY

## 2.1 Bromine

### 2.1.1 Overview of Bromine Industry

Over 80% of the domestic production of bromine occurs in southern Arkansas (Table 2.1-1). The major uses for bromine in the U.S. are shown in Table 2.1-2, which was compiled from numerous sources, none of which alone provides a detailed picture of bromine's use pattern. Despite the declining usage of ethylene dibromide (EDB) in gasoline, EDB is still responsible for nearly half of the total domestic bromine demand. At least 76 brominated organic chemicals were listed by the International Trade Commission as being produced commercially during 1978 (see Appendix A).

The flow of bromine and its compounds through the U.S. marketplace during 1979, according to the U.S. Bureau of Mines, is illustrated in Figure 2.1-1, including world production and imports. Table 2.1-3 depicts the industry for the 12-year period 1968 through 1979. The salient features of the 1979 domestic bromine industry according to the U.S. Bureau of Mines were (Table 2.1-3):

- The U.S. produced 65 percent of the world's bromine.
- U.S. exports were far greater than imports.
- Nearly half of the U.S. demand for bromine was supplied as the gasoline additive ethylene dibromide (48 percent), followed by fire retardants (29 percent), sanitation preparations (16 percent), and other uses (6 percent).

Several significant changes have occurred in the bromine industry over the last several years, the most important of which has been the decline in ethylene dibromide utilization as a gasoline additive.

Since the U.S. Environmental Protection Agency's gasoline lead phase-down program began in 1973, and its ban against the use of leaded gasoline in automobiles equipped with catalytic converters began sometime later, ethylene dibromide's use as a combustion-exhaust lead scavenger has declined substantially -- roughly 25% between 1974 and 1979 -- resulting in 60 x $10^6$ lb less bromine being used for EDB production in 1979 than in 1974. This situation, plus the addition of 200 x $10^6$ lb bromine production capacity (nameplate) during 1975 and 1976, left the bromine industry with a large excess production capacity for ethylene dibromide and bromine. (However, brine supply systems limit the actual capacity to considerably less than nameplate cpaacity, according to a major producer.) Industry sources indicated to Winzler and Kelly that there are no other sizeable products for which the excess EDB capacity can be used.

Table 2.1-1. Bromine-producing Plants in the United States (All Production from Well Brines)

| State & Company | County | Plant | Production Capacity ($10^6$ lb/y)[a] |
|---|---|---|---|
| Arkansas: | | | |
| Arkansas Chemicals, Inc. | Union | El Dorado | 50 |
| The Dow Chemical Co. | Columbia | Magnolia | 110 |
| Ethyl Corp. | Columbia | Magnolia | 160 |
| Great Lakes Chemical Corp. | Union | El Dorado | 105 |
| Great Lakes Chemical Corp. | Union | Marysville | 80 |
| Velsicol Chemical Corp.[b] | Union | El Dorado | 40 |
| Michigan: | | | |
| The Dow Chemical Co. | Mason | Ludington | 20 |
| The Dow Chemical Co. | Midland | Midland | 85 |
| Morton Chemical Co. | Manistee | Manistee | 5 |
| | | Total | 655 |

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Source: U.S. Bur. Mines, 1980, except as noted otherwise.

[a] Source: Lyday, 1980.

[b] Velsicol's bromine-production facilities were purchased by Great Lakes in the summer of 1981 (Chem. Mark. Rep., 20 July 1981, p. 3).

Table 2.1-2. U.S. Demands for Bromine, 1979

| Compound | Use | Demand ($10^6$ lb bromine) | % of Total |
|---|---|---|---|
| Ethylene Dibromide (EDB)[a] | Gasoline additive, fumigant | 183 | 45 |
| Various[b] | Fire retardants | 111 | 27 |
| Calcium Bromide[c] | Well-drilling fluid | 48 | 12 |
| Methyl Bromide[d] | Fumigant | 37 | 9 |
| Bromine Chloride[e] | Water disinfectant | 17 | 4 |
| Elemental Bromine[f] | Chemical manufacturing, water disinfection, pulp bleaching, others | 9 | 2 |
| | | 405 | 100 |

---

[a] Source: Table 2.1-3

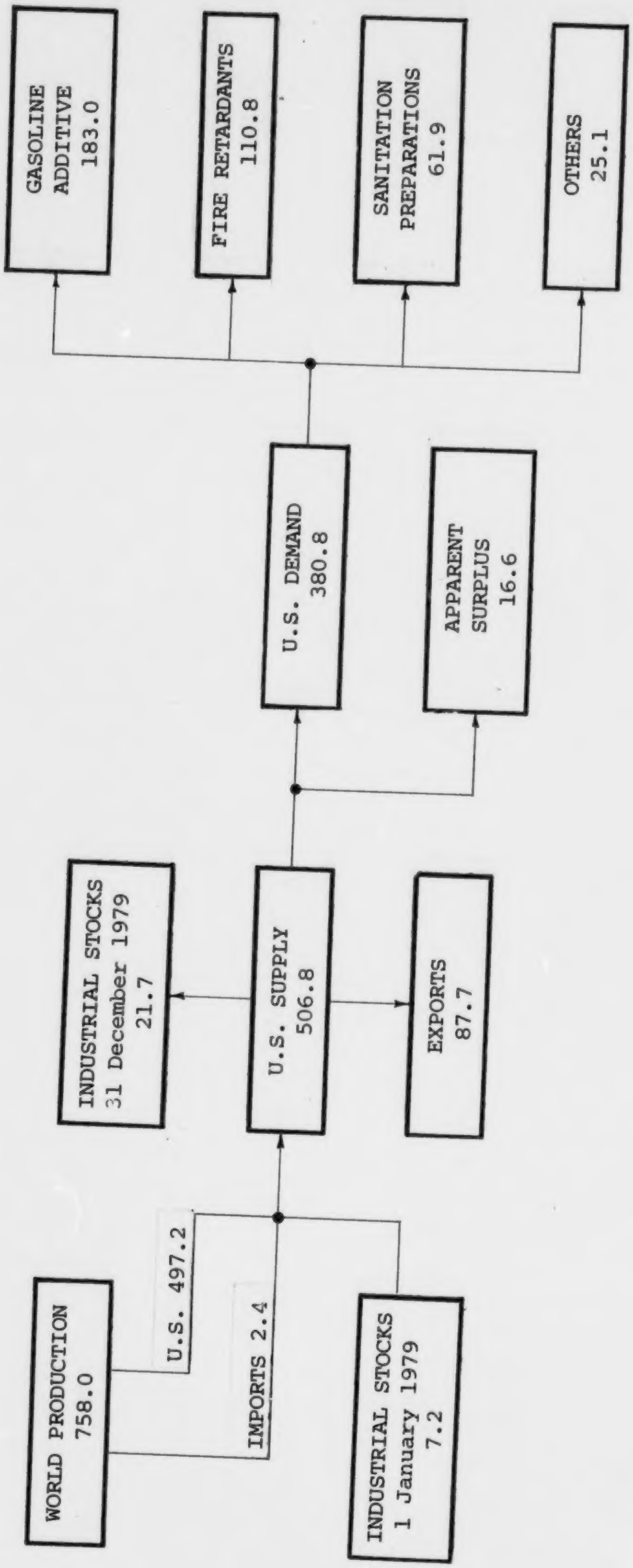
[b] Source: Table 2.1-3, but difficult to estimate. See section on fire retardants.

[c] Source: Anonymous major producer.

[d] Source: 44 x $10^6$ lb sold (U.S. Bur. Mines, 1980) minus roughly 7 x $10^6$ lb exported (SRI, 1980).

[e] Source: See Section 2.6.2

[f] SRI (1980) stated a demand of 53 x $10^6$ lb elemental bromine in 1978 for various uses, including chemical synthesis, and a demand of 64 x $10^6$ lb for fire retardants in 1977. Assuming that the Bureau of Mines' estimate of 111 x $10^6$ lb for fire retardants was correct, we assumed further that some of the stated 53 x $10^6$ lb elemental bromine demand was for various fire retardants. Therefore, we inflated 64 x $10^6$ lb at 7.5%/y for two years to estimate 1979 demand (67 x $10^6$ lb), and 44 x $10^6$ lb were transferred from the elemental bromine account (53 x $10^6$ lb) to the fire retardant account (67 x $10^6$ lb) to give 111 x $10^6$ lb for fire retardants, conforming to the Bureau of Mines' estimate. This manipulation left 9 x $10^6$ lb in the elemental bromine account.


WORLD PRODUCTION 758.0
U.S. 497.2
IMPORTS 2.4
INDUSTRIAL STOCKS 1 January 1979 7.2
INDUSTRIAL STOCKS 31 December 1979 21.7
U.S. SUPPLY 506.8
EXPORTS 87.7
U.S. DEMAND 380.8
APPARENT SURPLUS 16.6
GASOLINE ADDITIVE 183.0
FIRE RETARDANTS 110.8
SANITATION PREPARATIONS 61.9
OTHERS 25.1

SCHEMATIC OF DOMESTIC BROMINE SUPPLY AND DEMAND, 1979
(MILLIONS OF LBS; FROM TABLE 2.1-3)

Figure 2.1-1

Table 2.1-3. Bromine Supply and Demand Relationships, 1968 through 1979[a]

(Thousand pounds of bromine)

| | 1968 | 1969 | 1970 | 1971 | 1972 | 1973 | 1974 | 1975 | 1976 | 1977 | 1978[b] | 1979[b] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| World production | | | | | | | | | | | | |
| United States[1] | 304,500 | 335,240 | 349,748 | 355,946 | 386,864 | 418,250 | 432,094 | 407,163 | 460,061 | 433,818 | 446,500 | 497,200 |
| Rest of world[e] | 92,200 | 107,800 | 123,270 | 150,661 | 196,488 | [r]171,766 | [r]202,377 | [r]204,291 | 213,022 | 241,965 | 237,500 | 206,800 |
| Total[e] | 396,700 | 443,040 | 473,018 | 506,607 | 583,352 | [r]590,016 | [r]634,471 | [r]611,454 | 673,083 | 675,783 | 684,000 | 758,000 |
| Components of U.S. supply: | | | | | | | | | | | | |
| Domestic sources | 304,500 | 335,240 | 349,748 | 355,946 | 386,864 | 418,250 | 432,094 | 407,163 | 460,061 | 433,818 | 446,500 | 497,200 |
| Imports | (2) | 50 | 144 | 14 | 46 | 57 | 22 | 49 | 342 | 726 | 1,499 | 2,434 |
| Industry stocks, Jan. 1[e] | 29,000 | 30,000 | 33,000 | 33,000 | 32,000 | 30,993 | 21,000 | 21,000 | 24,000 | 24,000 | 24,000 | 7,200 |
| Total U.S. supply | 333,500 | 365,290 | 382,892 | 388,960 | 418,910 | 449,300 | 453,116 | 428,212 | 484,403 | 458,544 | 471,998 | 506,834 |
| Distribution of U.S. supply: | | | | | | | | | | | | |
| Industry stocks Dec. 31[e] | 30,000 | 33,000 | 33,000 | 32,000 | 30,993 | 21,000 | 21,000 | 24,000 | 24,000 | 24,000 | 7,200[c] | 21,700[c] |
| Exports | 7,000 | 5,090 | 8,014 | 20,000 | 30,007 | 55,000 | 69,346 | 65,233 | 67,024 | 59,440 | 94,300 | 87,700 |
| Industrial demand | 297,500 | 330,200 | 341,878 | 335,960 | 356,903 | 363,307 | 362,770 | 341,979 | 393,379 | 375,104 | 375,800 | 380,800 |
| Apparent surplus (+), deficit (-) supply | -1,000 | -3,000 | — | +1,000 | +1,007 | +9,993 | — | -3,000 | — | — | -5,300 | +16,634 |
| U.S. demand pattern[e] | | | | | | | | | | | | |
| Gasoline additive | 207,500 | 230,000 | 242,733 | 225,800 | 269,300 | 253,800 | 240,000 | 216,000 | 241,000 | 226,000 | 220,500 | 183,000[c] |
| Sanitation preparations | 41,600 | 45,900 | 47,863 | 47,160 | 35,800 | 37,300 | 36,300 | 37,400 | 38,500 | 39,700 | 35,800[c] | 61,900[c] |
| Fire retardants | 14,800 | 15,800 | 17,094 | 23,600 | 25,100 | 52,300 | 56,000 | 48,000 | 58,000 | 64,000 | 70,000[c] | 110,800[c] |
| Other | 33,600 | 38,500 | 34,188 | 39,400 | 26,703 | 19,907 | 30,470 | 40,579 | 55,879 | 45,404 | 49,500[c] | 25,100[c] |
| Total U.S. primary demand | 297,500 | 330,200 | 341,878 | 335,960 | 356,903 | 363,307 | 362,770 | 341,979 | 393,379 | 375,104 | 375,800 | 380,800 |

e Estimated
r Revised
1 Elemental bromine sold as such or used in the preparation of bromine compounds by primary producers.
2 Less than 1/2 unit.
a Source: U.S. Bur. Mines, 1979, except as otherwise noted.
b Source: U.S. Bur. Mines, 1980, except as otherwise noted.
c Source: Lyday, 1980.

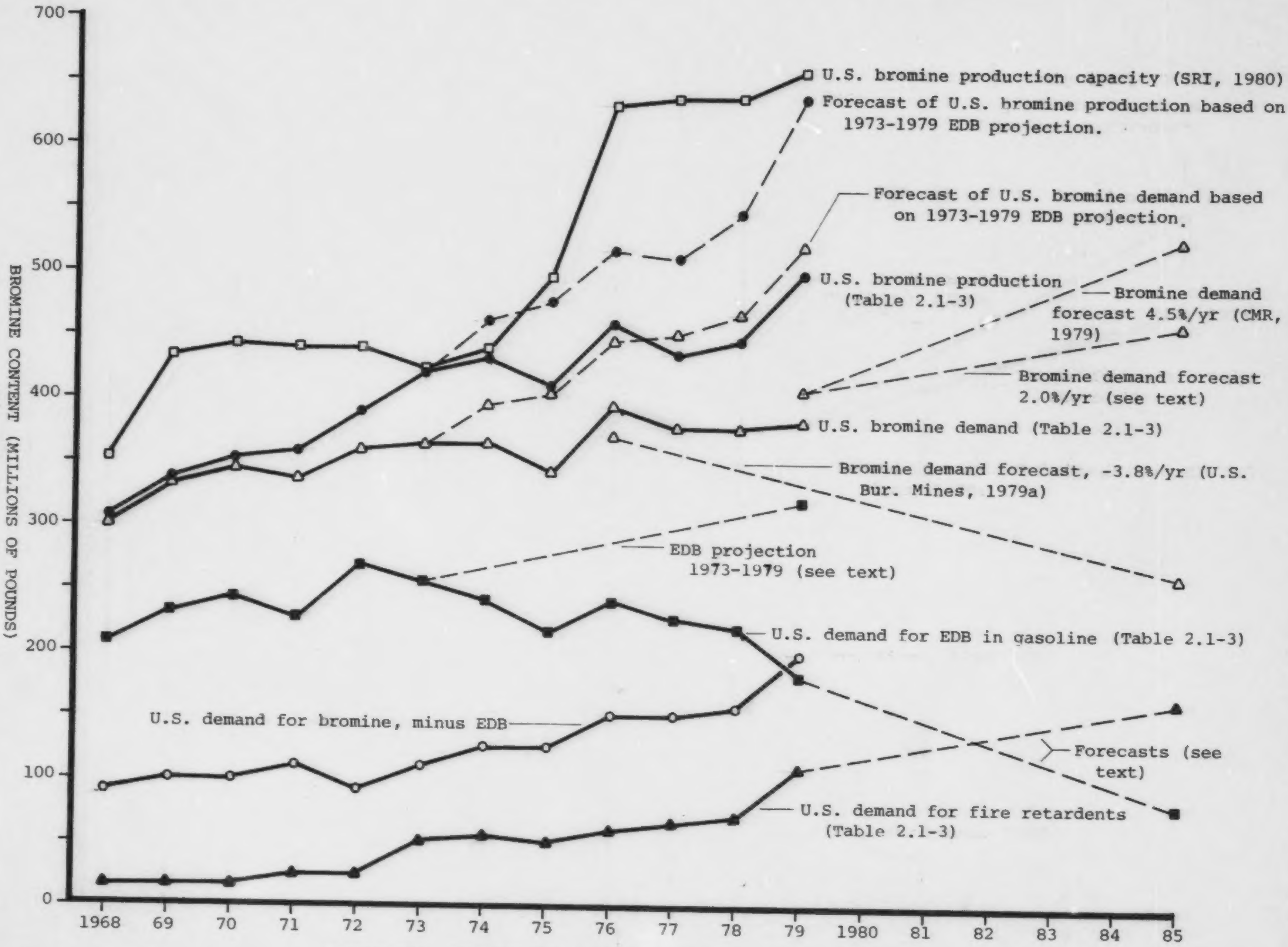
In Table 2.1-3, bromine-based fire-retardant chemicals show a moderately strong and steady increase in demand over the years, with a dramatic increase of 58 percent from 1978 to 1979 (70 x $10^6$ lb Br to 110.8 x $10^6$ lb Br). These data are in rough agreement with one other source, but they are not in line with other estimates, which indicate that bromine-based fire-retardant production is between 30 x $10^6$ and 50 x $10^6$ lb/yr (not as bromine content). Because of the increasing demand for fire retardants, the virtual elimination of the production and use of the brominated flame retardants "tris" and polybrominated biphenyls in the U.S. during the 1970's did not cause a dip in the overall demand for fire retardants.

The demand for calcium bromide has grown tremendously since its introduction as a well-drilling fluid in 1972. Since 1976, domestic production increased from nearly zero to over 100 x $10^6$ lb (42% bromine content) in 1978. This increased demand stems from the oil and gas industry's efforts to increase production.

"Sanitation preparations" (Table 2.1-3), which include bromine chloride and elemental bromine used as water disinfectants and methyl bromide and ethylene dibromide used as fumigants (Lyday, 1980), experienced a diminishing demand until 1979, when domestic demand increased 73 percent over the 1978 level. Virtually all of the "sanitary preparations" group in Table 2.1-3 can be accounted for by the fumigants methyl bromide and ethylene dibromide through 1978. In 1979, a new facility with a production capacity for bromine chloride of 30 x $10^6$ lb/yr (21 x $10^6$ lb bromine per yr) began operating, helping to account for the large increase in demand.

Figure 2.1-2 depicts domestic production, consumption, and capacity trends for bromine from 1968 through 1979 and forecast to year 1985. The historical data show a gradual increase in production and demand for bromine; a widening in the difference between production and demand, indicating increased exports in the 1970's; a moderately high increase in the demand for fire retardants and decrease for EDB; and sharp increases in production capacity during 1975 and 1976.

A projection of EDB demand between 1973 and 1979, assuming that leaded gasoline consumption had not been diminished by EPA regulations or by the Arab oil embargo and subsequent price escalation, was made simply by fitting the linear regression line to the data for 1968 through 1973 (Table 2.1-3) and extending the line to 1979. The difference between the forecast and the actual EDB demand line was added to the actual bromine demand and production lines to simulate their behavior had leaded gasoline consumption not declined. Thus, Figure 2.1-2 shows that there would likely have been only a small excess bromine production capacity by 1979 had EDB consumption not been diminished by EPA regulations governing the use of leaded gasoline or by gasoline shortages and price increases. Projecting EDB in proportion to the actual consumption



PRODUCTION, CONSUMPTION, AND CAPACITY TRENDS FOR BROMINE

Figure 2.1-2

of motor-vehicle fuels (U.S. Bur. Census, 1980) yields a similar result, but the projection is shifted downward 20 x $10^6$ to 25 x $10^6$ lb by 1978. Excess capacity would have still been small.

Five forecasts to 1985 of bromine or brominated compound demand are depicted in Figure 2.1-2. The upper demand line is based on the forecast that bromine demand will grow 4 to 5%/yr (CMR, 1979). The 1979 level (from Table 2.1-2) was increased at 4.5%/yr, compounded annually.

The middle forecast for bromine in Figure 2.1-2 was based on the following assumptions:

1. Assume that gasoline demand will fall at 1.4%/yr from roughly 110 x $10^9$ gal/yr (U.S. ITC, 1979) to 90 x $10^9$ gal in 1985.

2. Assume that by 1985 the average lead content of gasoline will be 0.8 g/gal and that bromine is present at half the concentration of lead.

3. Assume that bromine demand for fire retardants will increase at 7%/yr (see section on fire retardants) and that the base demand is 111 x $10^6$ lb (Table 2.1-2).

4. Assume that bromine chloride demand roughly doubles to 40 x $10^6$ lb/yr. On a compounded annual basis, this would be 15%/yr.

5. Assume calcium bromide demand will increase at 15%/yr (see Section 2.5.2) to 111 x $10^6$ lb bromine content by 1985.

6. Assume that methyl bromide demand will grow at 4.5%/yr (see Section 2.3.2) to 48 x $10^6$ lb bromine content by 1985.

7. Assume that all other uses for bromine will grow at 4.5%/yr to 12 x $10^6$ lb in 1985. The overall forecasted growth rate for bromine of 4 to 5%/yr (CMR, 1979) was assumed to apply here.

From these assumptions, the following changes in demand were computed:

| | 1979 | 1985 |
|---|---|---|
| Ethylene dibromide | 183 x $10^6$ lb | 80 |
| Fire retardants | 111 | 166 |
| Calcium bromide | 48 | 111 |
| Methyl bromide | 37 | 48 |
| Bromine chloride | 17 | 40 |
| Elemental bromine | 9 | 12 |
| | 405 | 457 |

The change in bromine demand from 405 to 457 x $10^6$ lb in 6 yr is equivalent to an average growth rate of 2.0%/yr compounded annually, which is substantially below the estimate of 4 to 5% (CMR, 1979).

The demand forecast for bromine shown in Figure 2.1-2 was made by the U.S. Bureau of Mines (1979a) utilizing a computerized end-use analysis system that performs statistical regression analysis on historical consumption and macroeconomic data. Contingency analysis is employed to modify historical trends in light of current and anticipated developments likely to affect demand, such as the declining consumption of leaded gasoline. The resulting forecasted long-term attrition rate of 3.8%/yr in bromine demand is not likely to be realized. This forecast was included here to illustrate the pitfalls of long-range market forecasts.

The forecast for ethylene dibromide was made as part of the middle forecast of bromine demand in Figure 2.1-2 discussed above. This forecast could be altered somewhat by the outcome of a review of the lead phase-down rules reportedly to occur (Chem. Engr. News, 17 Aug 1981, p. 7).

Bromine demand for fire retardants was assumed to grow at 7%/yr compounded annually, a compromise among various published estimates (see Section 2.4.2).

Forecasts of bromine demand by end use to the year 2000 were prepared recently by the Bureau of Mines. Table 2.1-4 shows these forecasts, along with 1978 actual demand and the 1985 forecasts prepared by Winzler and Kelly discussed above. The highest growth rate to year 2000 is forecast for "other" uses, which can be accounted for in large part by calcium bromide drilling fluids.

A marked apparent discrepancy between the 1985 and 2000 forecasts exists for fire retardants. Winzler and Kelly's 1985 forecasted demand for fire retardants exceeds the Bureau of Mines' year 2000 probable forecast. The average growth rate for fire retardants of 3.7%/yr applied to the 1978 demand of 70.0 x $10^6$ lb/yr for the 21-year period 1979 through 2000, inclusive, yielded 150 x $10^6$ lb demand for year 2000 (Table 2.1-4). However, the 1979 demand for fire retardants was 111 x $10^6$ lb bromine, and inflating this value by 3.7%/yr for 20 years yields a demand for fire retardants of 229 x $10^6$ lb bromine in year 2000, much higher than the Bureau of Mines' forecast. Therefore, we feel that the Bureau of Mines' probable forecast for fire retardants is low.

Barring severe economic depression, we see no reason why the overall growth in bromine demand should not be around 2%/yr through year 2000, which would yield a total demand for bromine of 570 x $10^6$ lb/yr, somewhat higher than the Bureau of Mines' estimate.

Table 2.1-4. Forecasts of Bromine Demand by End Use to Year 2000[a]
(Million Pounds)

|  |  |  | 2000 Contingency forecast for United States |  |  |  |
|---|---|---|---|---|---|---|
|  |  |  | Forecast range |  |  |  |
| End Use | 1978 | 1985 Contingency Forecast[b] | Low | High | Probable | (% Annual Growth)[e] |
| Petroleum | 220.5 | 80 | 10 | 150 | 75 | -4.8 |
| Sanitary preparations | 35.8 | 88[c] | 65 | 150 | 100 | 4.8 |
| Fire retardants | 70.0 | 166 | 50 | 150 | 150 | 3.5 |
| Other | 49.5 | 123[d] | 30 | 200 | 175 | 5.9 |
| Total | 375.8 | 457 | 155 | 650 | 500 | 1.3 |

---

[a] Source: Lyday, 1980a, unless noted otherwise.

[b] Source: Winzler and Kelly forecast, Section 2.1.1.

[c] "Sanitary preparations" includes methyl bromide and bromine chloride.

[d] "Other" uses includes calcium bromide and elemental bromine.

[e] Compounded annual rate for the 22-year period 1979 through 2000, calculated by Winzler and Kelly.

While the bromine production in the U.S. has increased modestly over the years, production in Israel has more than doubled since 1976, although U.S. production was still five-fold greater than Israel's in 1979 (Table 2.1-5). Moreover, in an effort to boost exports, Israel plans on doubling its bromine production from 53,000 tonnes (116 x 10$^6$ lb) in 1980 to 100,000 tonnes (220 x 10$^6$ lb) per year by 1984 (European Chemical News, 1 January 1980, p. 28).

Imports increased greatly during 1978 and 1979 (Table 2.1-6), although they are still only 1% or less of domestic consumption. During 1979, approximately 99% of the accounted-for imports (i.e., those shown in Table 2.1-6) were from Israel.

Arab Potash Company plans to construct a potash recovery plant in Jordan using brines from the Dead Sea. The plant is expected to be operational by the spring of 1983, and it may be expanded to produce bromine, sodium chloride, and magnesia (Chemical Week, 6 August 1980, p. 45). The expected bromine-production capacity is 66 x 10$^6$ lb/yr (Lyday, 1980a).

Exports increased significantly over 1977, although declining 6% from 1978 to 1979 (Table 2.1-7). Exports represented approximately 18 percent of the bromine produced in the U.S. during 1979. Israel is aggressively pursuing a program of increased production of bromine and bromine-based chemicals for foreign markets. Because bromine in its lead-lined shipping containers is heavy, and therefore costly to transport, Israel will likely be able to capture a portion of U.S. exports to areas that are closer to Israel than to the U.S. Nevertheless, U.S. producers feel that their foreign markets will remain strong. Bromine, being toxic and corrosive, requires special containers for shipping, including lead-lined tank cars, metal drums, and glass jars, which are regulated by the Interstate Commerce Commission (Lyday, 1981). The strength of the recent export market may be due to the approval of a lightweight container for shipping bromine (SRI, 1980). Also, to increase profits and safety, producers tend to ship bromine derivatives rather than bromine itself, according to a major producer.

### 2.1.2 Environmental Considerations for the Bromine Industry

Bromine is a dark, reddish-brown liquid that is a strong oxidizing agent and produces irritating fumes. With a permissible occupational 8-hr time-weighted average concentration of 1 ppm (NIOSH/OSHA, 1978), bromine is considered highly toxic.

Elemental bromine ($Br_2$) is produced from brines with a high bromide content by oxidizing the bromide to $Br_2$ with chlorine ($Cl_2$). The $Br_2$ is purified by distillation (Lowenheim and Moran, 1975). Waste brine is reinjected to the earth.

Table 2.1-5. World Production of Bromine by Country

(Thousand Pounds)

| Country[1] | 1976 | 1977 | 1978[p] | 1979[e] |
|---|---|---|---|---|
| France | 33,466 | 34,326 | 35,000[e] | 35,000 |
| Germany, Federal Republic of | 9,158 | 8,236 | 8,583 | 8,600 |
| India[e] | 600 | 620 | 660 | 600 |
| Israel | 46,100 | 69,450 | 76,170 | 100,000 |
| Italy | 1,230[r] | 1,300[e] | 1,300[e] | 1,300 |
| Japan[e] | 26,500 | 26,500 | 26,500 | 26,000 |
| Spain[e] | 900[r] | 900 | 900 | 900 |
| U.S.S.R.[e] | 30,000 | 33,000 | 33,000 | 33,000 |
| United Kingdom | 65,928[r] | 54,500 | 55,000 | 55,000 |
| United States[2] | 468,800[r] | 433,900 | 446,500 | 497,200 |
| Total[3] | 682,000 | 663,000 | 684,000 | 758,000 |

---

e Estimate
p Preliminary
r Revised
1 In addition to the countries listed, several other nations produce bromine, but output data are not reported and available general information is inadequate for formulation of reliable estimates of output levels.
2 Sold or used by producers.
3 Data does not add to totals shown because of independent rounding.

Source: U.S. Bur. Mines, 1980.

Table 2.1-6. Imports of Bromine and Bromine Compounds

(Thousand pounds and thousand dollars. Numbers in parentheses are bromine content.)

| | 1977 | | 1978 | | 1979 | |
|---|---|---|---|---|---|---|
| | Quantity | Value | Quantity | Value | Quantity | Value |
| Elemental bromine | 517 (517) | 102 | 669 (669) | 102 | 34 (34) | 5 |
| Potassium bromide | 89 (60) | 56 | 119 (80) | 84 | 794 (534) | 536 |
| Sodium bromide | 106 (82) | 60 | 320 (249) | 175 | 2,190 (1,702) | 1,056 |
| Ethylene dibromide | 79 (67) | 22 | 589 (501) | 102 | 193 (164) | 33 |
| Total | 791 (726) | 240 | 1,697 (1,499) | 463 | 3,211 (2,434) | 1,630 |

Source: U.S. Bureau of the Census data, taken from U.S. Bur. Mines, 1980.

Table 2.1-7. Exports of Bromine and Bromine Compounds by Primary U.S. Producers

(Thousand pounds and thousand dollars)

| Year | Elemental Bromine | | Bromine Compounds | | | Total Bromine |
|---|---|---|---|---|---|---|
| | Quantity | Value | Gross Weight | Contained Bromine | Value | |
| 1976 | 4,400 | 900 | 74,100 | 62,600 | 29,200 | 67,000 |
| 1977 | 5,400 | 1,100 | 64,400 | 54,100 | 27,300 | 59,500 |
| 1978 | 6,400 | 1,300 | 106,000 | 87,900 | 38,500 | 94,300 |
| 1979 | 10,100 | 2,100 | 92,800 | 77,600 | 35,500 | 87,700 |

---

Source: U.S. Bur. Mines, 1980.

During the production, handling, and utilization of bromine, some escapes to the atmosphere. It has been detected in the air near production facilities (Pellizzari, et al. 1978a), and bromine was found accumulating in pine needles and twigs growing in such locations (Tainter and Bailey, 1980).

However, the greatest potential environmental hazard may not be with bromine itself, but rather with low-level or accidental exposure to specific brominated chemicals that are potentially carcinogenic or teratogenic. Brominated animal carcinogens include ethylene dibromide, "tris," and vinyl bromide. Extrapolating high-dose (or even low-dose) animal data to the effects of a substance on humans at low-level exposures is controversial. These considerations are addressed in the substance-specific sections of this report that follow.

## 2.2 Ethylene Dibromide

### 2.2.1 Introduction

Ethylene dibromide (1,2-dibromoethane) is produced in large quantities for use as an additive to leaded gasoline, where it binds lead in the combusted gases and prevents the lead from being deposited in the combustion chamber of the motor vehicle engine. Ethylene dibromide (EDB), alkyl lead, and other additives constitute "motor mix," which is then shipped to petroleum refiners. Smaller portions of the ethylene dibromide produced is used as a fumigant, and EDB is also said to be used in vinyl bromide production, as a solvent, and in plastics (Mara and Lee, 1978).

The historical data for the consumption of bromine (U.S. Bur. Mines, 1980) and lead (Ryan and Hague, 1977) in gasoline show that bromine is present (as EDB) at roughly half the concentration of lead. This estimation is confirmed by the range of EDB concentrations stated by McDermott and Killiany (1978) (80 to 150 ppm by volume = 0.66 to 1.23 g/gal). Thus, the EDB concentration stated by Johns (1976) (0.05% by volume = 3.4 g Br/gal) is much too high. The 1978 lead content of 1.3 g/gal (U.S. ITC, 1979) translates to 0.65 g Br/gal.

EDB is a colorless, nonflammable, dense liquid with a sweet odor. The characteristics of EDB are summarized in Table 2.2-1.

EDB is produced in an EDB solution by the reaction of ethylene and bromine ($CH_2=CH_2 + Br_2 = CH_2Br - CH_2Br$), and the product EDB is purified by distillation (Lowenhein & Moran, 1975). Potential sources of emissions in such a system include contaminated cooling water (from leaky heat exchangers), the distillation column, and leaky gaskets, piping, and storage facilities.

### 2.2.2 Production and Consumption

Estimates of domestic ethylene dibromide production vary appreciably from one source to another. Table 2.2-2 presents

Table 2.2-1. Chemical and Physical Properties of Ethylene Dibromide

| | |
|---|---|
| Chemical Formula | $BrCH_2CH_2Br$ ($C_2H_4Br_2$) |
| Synonyms | 1,2-dibromoethane; ethylene bromide; EDB |
| CAS Registry No. | 106-93-4 |
| NIOSH RTECS No. | KH 92750 |
| Molecular Weight | 187.88 |
| Boiling Point, °C | 131.5 |
| Melting Point, °C | 9.3 (also reported as 9.1, 9.97, and 9.9 in various other sources) |
| Vapor Pressure, mm Hg | 11.0 @ 25°C; 17.4 @ 30°C[a] |
| Specific Gravity, liquid | 2.172 (water @ 4°C = 1) |
| Specific Gravity, vapor @ 20°C | 6.487 (air = 1) |
| Solubility | 0.43 g/100 g water @ 30°C; miscible in ethanol, ether, octanol[a], and most organic solvents. |
| Stability | Stable |
| Flammability | Nonflammable |
| Appearance | Colorless liquid |
| Heat of Vaporization | 46.2 cal/g |
| Corrosiveness | Vapor or liquid attacks many paints and some metals (especially aluminum) |
| Flash Point | None |
| Fire Point | None |
| Weight & Volume Conversions | 1 U.S. gallon = 18.11 lbs. = 8.23 kg<br>1 lb. liquid = 208 ml @ 25°C<br>1 oz/1000 $ft^3$ = 1 mg/liter = 1 $gm/m^3$<br>1 ppm = 7.69 $mg/m^3$<br>1 $mg/m^3$ = 130 ppb |
| Density of EDB in saturated air | 1.08 (air = 1) |
| Conc. of EDB in air at saturation | 1.3% by vol. @ 20°C |
| Refractive Index @ 20°C | 1.5379[a] |
| Odor | Sweet, like chloroform[a] |

---

Source: U.S. EPA, 1980, unless otherwise noted.

[a] Source: Mara and Lee, 1978.

Table 2.2-2. Estimated Ethylene Dibromide Production in the U.S. (millions of pounds)

| | Ethylene Dibromide | Bromine Content |
|---|---|---|
| 1974[a] | 332 | 282 |
| 1975[b] | 275 | 234 |
| 1976[c] | 201 | 171 |
| 1977 | 244[d]<br>280[e] | 207<br>238 |
| 1978 | 230[f]<br>259[e] | 196<br>220 |
| 1979 | 286[g]<br>215[h]<br>256[i] | 243<br>183<br>218 |
| 1980 | 176[i] | 150 |
| 1982 (projected) | 150[i] | 128 |

---

[a] Source: U.S. ITC, 1976.
[b] Source: U.S. ITC, 1977a.
[c] Source: U.S. ITC, 1977b
[d] Source: U.S. ITC, 1978
[e] Source: U.S. Bur. Mines, 1980. Amount sold by primary producers.
[f] Source: U.S. ITC, 1979
[g] Source: U.S. ITC, 1980
[h] Source: Lyday, 1980. Amount sold by primary producers.
[i] Source: Anonymous major producer, November 1980.

data collected from several sources. Despite the variation from year to year and from source to source, it is clear from the table that ethylene dibromide consumption has decreased considerably since 1974. This trend is attributable to the lead phase-down regulations of the U.S. Environmental Protection Agency that were promulgated originally on 6 December 1973 (38 Fed Reg 33734) under the Clean Air Act and to the utilization of catalytic converters on late model automobiles, which necessitates the use of unleaded gasoline. The decline in ethylene dibromide production has led to an excess of production capacity. A representative of one major producer estimated very roughly that producers were operating at 65 percent of nameplate capacity (i.e., the capacity at continuous operation at design capacity), that this fraction would continue to decline, and that the capacity had no alternate uses without very extensive plant modifications.

SRI (1980) reported the following production capacities as of June 1979:

| | $10^6$ lb/yr |
|---|---|
| Dow Chemical Co., Magnolia, Arkansas | 115 |
| Ethyl Corp., Magnolia, Arkansas | 150 |
| Great Lakes Chemical Corp., El Dorado, Arkansas | 50 |
| PPG Industries, Beaumont, Texas | 35 |
| | 350 |

Brine supply systems limit the actual capacity to considerably less than nameplate capacity, according to a major producer.

Recent estimates place EDB's consumption as a fumigant at roughly 15 x $10^6$ lb (U.S. EPA, 1980 and anonymous major producer). Other estimates differ greatly: 7 x $10^6$ lb (Chem. & Eng. News, 19 Dec. 1977, p. 3 and Wall St. Jour., 14 Dec. 1977, p. 4); 1.5 x $10^6$ lb (Brown et al. 1975b); and 1.6 x $10^6$ lb (Johns, 1976). EDB's use in California during 1979 amounted to 6.7 x $10^5$ lb (Calif. Dept. Food & Agric., 1980).

It was reported that EDB's use as a solvent and in other dispersive uses amounts to 29.3 x $10^6$ lb/yr and as a synthetic intermediate 16.3 x $10^6$ lb/yr (Johns, 1976). The "other dispersive uses" were not enumerated. We have found no confirmation of these estimates elsewhere, and we feel that they are likely highly overstated.

Imports of ethylene dibromide in 1979 were estimated to be only 193 x $10^3$ lb (Table 2.1-4). Exports of EDB as such are small, and Israel has most of the foreign market; however, according to one producer, a significant but undetermined amount of EDB is exported in gasoline antiknock mixtures along with alkyl lead compounds and ethylene dichloride. Brown et al. (1975) stated that imports and exports of EDB were negligible.

Production and consumption of ethylene dibromide are closely linked to the use of leaded gasoline. In late 1973, the U.S. Environmental Protection Agency promulgated lead phase-down rules that will result in gasoline having an average lead content of no more than 0.5 g/gal. Major refiners were required to meet this requirement by 1 October 1980, and small refiners will be in 1982 (Summerhayes, 1980). At a 1979 gasoline demand of roughly 110 x $10^9$ gallons and an average bromine content of 0.25 g/gal (half of the lead content), bromine demand for EDB lead scavenger would be 60 x $10^6$ lb, a 73% decline from the 1978 demand level of 220 x $10^6$ lb estimated by the Bureau of Mines (1980). However, since 1976 the allowed lead limit in gasoline has been 0.8 g/gal, yet because of waivers, the actual average concentration was around 1.3 g/gal in 1978 (U.S. ITC, 1979), indicating that the phase-down may be gradual. The lead phase-down rules are reportedly to be reviewed and possibly eased (Chem. Engr. News, 17 Aug. 1981, p. 7), so demand may not fall as much as expected.

Another important factor influencing the demand for leaded gasoline is the extensive use of catalytic converters on new automobiles. The converters are "poisoned" by lead, and the use of unleaded gasoline in automobiles equipped with catalytic converters is required by federal law. All 1980 model year and later automobiles in the U.S. (domestic and foreign) have a specification for unleaded gasoline. Heavy trucks and vans need not use unleaded fuel. This trend would eventually result in very low average lead concentrations in gasoline even without the lead phase-down rules. However, research is underway to develop lead-tolerant catalytic converters, which, if successful, could reverse this trend (Summerhayes, 1980).

The Bureau of Mines is forecasting a probable utilization of 2.2 x $10^8$ lb lead in gasoline by the year 2000, compared to a production of 3.9 x $10^8$ lb in 1978. Both figures include estimated exports of 1.1 x $10^8$ lb (Rathjen, 1980). This 44-percent decline in alkyl-lead additive consumption by year 2000 compared to year 1978 should also be experienced by ethylene dibromide production for use as a lead scavenger in this scenario. A 44-percent reduction in the 1978 consumption of bromine in gasoline of 220 x $10^6$ lb (U.S. Bur. Mines, 1980) leaves 123 x $10^6$ lb being used in year 2000 if the lead consumption forecast is correct, double the demand allowed by the lead phase-down standard (see above).

EDB's use as a pesticide is expected to grow as a substitute for dibromochloropropane (DBCP), which has largely been banned. For example, EPA recently approved EDB for use on soil during soybean planting, one of the former uses for DBCP (Chem. Mark. Rep., 9 Mar. 1981, p. 27). On the other hand, EPA is proposing to cancel registrations on some relatively minor uses of EDB. According to EPA, nearly all of the pesticidal use of EDB is as a pre-plant soil fumigant, and EPA is not proposing to cancel registrations for such uses (U.S. EPA, 1980), which has encouraged Great Lakes Chemical Corporation in its plans to expand EDB's use as a soil fumigant (Chem. Mark. Rep., 8 Dec 1980, p. 5). (A major producer stated the major pesticidal use was indeed as a soil fumigant, but not a pre-plant fumigant.) However, should EDB prove to be a groundwater contaminant like DBCP, cancellation could result. Therefore, the direction that the EDB pesticide market will take in the long run is uncertain, but it will likely increase during the next few years.

Ethylene dibromide is under consideration by EPA for regulation under Section 112 of the Clear Air Act (National Emission Standards for Hazardous Air Pollutants), (Chem. Engr. News, 24 Mar. 1980, p. 18). Such regulation would result in an emission standard for ethylene dibromide, or, where this is infeasible, design, equipment, work practice, or operational standards may be imposed. However, vinyl chloride is under NESHAP regulation, and its domestic production and consumption remains very high. An industry spokesman felt that regulation of EDB under NESHAP would not significantly affect EDB production, considering that facilities already must meet a 20 ppm occupational exposure limit. In any case, the promulgation of emission standards will likely not occur for several years, if ever (Shell, 1981). However, under a proposed EPA rule to control volatile organic compound emissions, new stationary sources would be required to implement a leak detection and repair program to reduce EDB emissions from valves; install certain equipment to reduce emissions from pumps, compressors, sampling connections, and open-ended lines; and prevent leaks from safety relief valves during normal operations (46 Fed Reg 1136, 5 Jan. 1981). This proposal was vigorously attacked by the Synthetic Organic Chemical Manufacturers Association on the grounds that its costs would far outweigh the resulting benefits (Chem. Engr. News, 9 Mar. 1981, p. 14).

The regulatory environment for EDB producers is poor at this time. Faced with large excesses of production capacity, yet fearful that any existing or new uses of EDB could be banned, producers are unwilling to expend much effort on developing new markets (anonymous major producer, Nov. 1980), helping to ensure the depressed state of the EDB portion of the bromine industry.

### 2.2.3 Emissions and Atmospheric Concentrations

The major sources of airborne emissions of EDB are manufacturing and "motor mix" formulating facilities, gasoline service stations, petroleum refineries where leaded gasoline is formulated, gasoline storage and distribution facilities, and motor vehicles (Mara and Lee, 1978). Humans are also exposed via fumigation operations and contaminated food from space fumigation (U.S. EPA, 1980).

Because little emissions data were available, Mara and Lee (1978) estimated emission rates for EDB based on previously developed factors for benzene or from air monitoring data. For EDB production and formulating plants, the ambient air monitoring data were used. Within 100 m of the Dow Chemical Company plant in Magnolia, Arkansas, a concentration of 100 μg EDB/m$^3$ (13 ppb) was measured. Mara and Lee (1978) assumed that 20 μg/m$^3$ (3 ppb) was a reasonable ambient concentration at 100 m, considering wind variability.

Using the simple dispersion model in Appendix B, an emission rate of 0.07 g/s was back-calculated from the 20 μg/m$^3$ level at 100 m. Assuming that this rate of emission occurred continuously during plant operation and that the plant was operated 90% of the time, 4376 lb EDB would be emitted per year. Capacity at Dow's plant was reported to be 14 x 10$^6$ lb/yr. Assuming a production rate of 85% of capacity, the calculated emission rate is 0.04% of the estimated production rate, which is quite low. Problems with this approach include: 1) the monitoring data (2 4-hr samples) are likely not representative of meteorological or plant operational conditions; and 2) assumes that the monitor was located on the center line of the plume.

Data on environmental concentrations of EDB, in addition to those used by Mara and Lee (1978), are available in the work of Pellizzari et al. (1978a). This more recent work demonstrated a maximum airborne EDB concentration of 271 μg/m$^3$ (35 ppb) at Great Lakes Chemical Corp. near El Dorado, Arkansas. This measurement was made approximately 200 yd from the organic synthesis facility. The maximum concentration measured at Parker's Chapel, which is located about 1 km from Great Lakes Chemical Corp. was 1.26 g/m$^3$ (164 ppt). During this measurement, the wind blew largely from the direction of Great Lakes Chemical.

Exposure to EDB at gasoline self-service stations was based on measurements of benzene in the breathing zones of persons filling their tanks. Conversion from benzene concentrations to EDB concentrations was based on EDB content of gasoline and vapor pressure. The results are shown in Table 2.2-3.

Based on an emission factor of lead from gasoline, Mara and Lee (1978) estimated that 3.9 x 10$^{-4}$ g EDB was emitted per gallon of gasoline pumped at the station. From this, they estimated population exposures in the vicinity of service stations (see Table 2.2-3).

Based on an emission factor for benzene at petroleum refineries, Mara and Lee (1978) estimated an EDB emission rate of 3.3 x 10$^{-7}$ kg/m$^3$ (1.3 x 10$^{-6}$ g/gal; 2.8 x 10$^{-9}$ lb/gal) for gasoline bulk loading facilities, which were thought to be the major sources of emissions from refineries. From this, they estimated population exposures (Table 2.2-3).

Based on an emission factor for benzene emissions from the storage of gasoline at gasoline bulk-storage facilities (not at refineries) were estimated to be 1.77 x 10$^{-7}$ kg EDB per m$^3$ gasoline (6.8 x 10$^{-7}$ g/gal; 1.5 x 10$^{-9}$ lb/gal) and 5.94 x 10$^{-6}$ g/s for the average storage terminal. Population exposures were estimated to be negligible (Mara and Lee, 1978).

Emissions resulting from gasoline transfers at bulk-storage facilities (not at refinery) were estimated, based on an emission factor for benzene, to be 3.65 x 10$^{-5}$ g EDB/s for the average facility. Population exposures were estimated to be negligible

Table 2.2-3. Summary of Human Exposures to Atmospheric Ethylene Dibromide from Emission Sources

| | Population Exposed to Ethylene Dibromide Concentrations (ppt)[a] | | | | | | Exposure Comparison Among Sources[c] ($10^6$ person-ppt) | | |
|---|---|---|---|---|---|---|---|---|---|
| 8-Hour Worst Case: | 10.0-50.0 | 50.1-100.0 | 100.1-200.0 | 200.1-400.0 | >400.0 | Total[b,c] | | | |
| Annual Average: | 1.0- 5.0 | 5.1- 10.0 | 10.1- 20.0 | 20.1- 40.0 | >40.0 | | c. 1975 | 1980[f] | 2000[f] |
| **Source** | | | | | | | | | |
| Manufacturing and Formulating | 580,000 | 250,000 | 160,000 | 99,000 | 84,000 | 1,200,000 | 14 | 11 | 4.9 |
| Gasoline Service Stations | | | | | | | | | |
| 1. People Using Self-Service | | | | | d | 30,000,000 | 1.3 | 1.0 | 0.46 |
| 2. People Living in the Vicinity | 100,000,000 | 10,000,000 | | | | 110,000,000 | 380 | 280 | 130 |
| Petroleum Refineries | 2,000,000 | 170,000 | 53,000 | 16,000 | 3,000 | 2,200,000 | 8.7 | 6.5 | 3.0 |
| Storage and Distribution | e | | | | | | | | |
| Urban Exposures - Automotive | 24,000,000 | | | | | 24,000,000 | 72 | 54 | 25 |
| Total | | | | | | | 480 | 360 | 170 |

[a] To convert to mcg/$m^3$, divide each exposure level by 130.

[b] Mara and Lee (1978) stated that population estimates are not additive vertically because some double counting may exist. However, we feel that "double counting" is simply adding exposures from the multiple sources and is valid.

[c] Totals are rounded to two significant figures.

[d] Estimated at 260 ppt for 1.5 hr/yr/person.

[e] Estimated at <<1.0 ppt annual average

[f] Estimated exposures reduced by 25 percent and 65 percent to account for diminished EDB utilization between 1975 and 1980, and 1975 and 2000, respectively, a Winzler and Kelly manipulation (see Section 2.1.1). They were not adjusted to account for the manufacturing and formulating capacities being used by Mara and Lee (1978) rather than actual production rates.

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Source: Mara and Lee, 1978, except as noted otherwise.

(Mara and Lee, 1978). EPA recently proposed rules to reduce emissions of volatile organic compounds, which would include EDB, from new, modified, or reconstructed tank-truck loading racks at bulk gasoline terminals (45 Fed Reg 83126, 17 Dec. 1980).

Mara and Lee (1978) estimated an automobile emission rate of 0.0063 g EDB/gal leaded gasoline used, and assuming that 100% of the automobiles used leaded gasoline, ambient concentrations and population exposures were estimated for c. 1975 (Table 2.2-3). The assumptions result in a high emission estimate because the emission rate was for pre-1972 automobiles, whereas controls to carburetor emissions were implemented in 1972, and the use of leaded gasoline in new cars was required beginning in 1975 (ibid, p. 58). In 1976, 20% of the gasoline consumed in the U.S. was unleaded (ibid., p. 23).

Table 2.2-3 summarizes the results of SRI's study of nationwide exposures to airborne EDB. Exposures to persons residing near gasoline service stations was estimated to result in the highest exposure (in person-ppt). In this situation, many persons are exposed to low concentrations. Person-ppt is the product of number of persons exposed and concentrations to which they are exposed. It is a measure of aggregate exposure, and its use is illustrated in Section 2.2.9.

### 2.2.4 Environmental Fate

Water

Pellizarri et al. (1978a) measured EDB in surface water on the Great Lakes Chemical Corp. site near El Dorado, Arkansas at a maximum concentration of 620 g/kg (620 ppb). Little other information was found on the environmental fate of EDB in water. In one review, it was reported that the rate of hydrolysis is very slow (half life of roughly $10^5$ days at pH 10 and $10^8$ days at pH 7), the products being glycol and bromoethanol (Brown et al., 1975b). If these reported half-lives (274 to 3 x $10^5$ years!) are accurate, EDB would be very stable in the aqueous environment. However, this report may be erroneous, for another review of the same data reported a hydrolysis half-life of 5 to 10 days, the reaction being favored by acidic conditions (Johns, 1976). Although little environmental data are available, a hydrolytic half-life of 5 to 10 days would likely be sufficient to prevent its accumulation in the aqueous environment under light loading conditions.

We have found no data on the propensity for EDB to bioaccumulate or biograde in water environments, although it was reported that in humans, EDB is partially decomposed in the body (Johns, 1976) and that it was degraded by soil fungi (Brown et al., 1975b), indicating that biodegradation in water and sediment is likely.

Because of EDB's moderate vapor pressure (11 mm Hg at 25°C), it would have a tendency to evaporate from water to a significant extent. The propensity of EDB to oxidize chemically or photolytically in water is unknown to us.

Like dibromochloropropane (Section 2.8.4), EDB could contaminate groundwater via soil fumigation. EPA proposed that registrants who apply EDB to soil be required to determine if such contamination occurs (see Section 2.2.9).

## Soil

Brown et al. (1975b) reported that EDB is degraded by soil fungi, although the degradation products were not reported. In one study, EDB was stable in soil for 2 weeks, but in another, a sterilized and reinoculated soil/water culture degraded $5.75 \times 10^{-4}$ M EDB (108.1 mg/l) completely within 2 months at pH 7, reportedly forming ethylene and bromide (Kover, 1976).

The hydrolytic half-life of 5 to 10 days for EDB reported for aqueous solution (see previous section) is relevant to its fate in soil because the same reaction can occur there.

Whether EDB is leached from soil into groundwater is unknown (see previous section).

## Air

EDB is thought to be only mildly susceptible to attack by radicals, peroxides, and ozone, with half-lives of 100 days or more (Brown et al., 1975b; Johns, 1976). Its possible degradation products include vinyl bromide and bromoacetaldehyde (Brown et al. 1975b), at least one of which (vinyl bromide) is itself a hazardous substance.

We have found no discussions on the effects of EDB on stratospheric ozone. However, its reported moderate resistance to degradation in the troposphere would likely permit its entry into the stratosphere, where it would be subject to intense ultraviolet irradiation and oxidative conditions, perhaps leading to the formation of free bromine atoms, which could then react with ozone to decompose it. Because EDB is released to the atmosphere in small amounts compared to chlorinated compounds, its effects on stratospheric ozone are likely comparatively minor at this time. The effect of bromine on stratospheric ozone is discussed in Section 2.3.4 in relation to methyl bromide.

The combustion of EDB in leaded gasoline reportedly results in the formation and emission of methyl bromide (see section on methyl bromide emissions).

## Food

EPA reports that residues have not been detected on crops grown in EDB-treated soil at a detection limit of 1 ppb (U.S. EPA, 1980).

### 2.2.5 Health Effects

EDB is an irritant to the respiratory system, eyes, and skin. The occupational exposure limit is 20 ppm averaged over 8 hr, with 30 ppm as an acceptable ceiling, and a maximum peak of 50 ppm during any 5-min interval (NIOSH, 1975; NIOSH/OSHA, 1978). EDB is reportedly absorbed readily through the lungs, skin, and gut of mammals. It is excreted by the lungs, metabolized in the body, and bromine is excreted in the urine (Johns, 1976).

Because the highest outdoor concentration of EDB measured to date is roughly 1000-times lower than the established occupational exposure level, there is little cause for concern over non-carcinogenic or non-teratogenic effects, except in the case of spills or other accidental situations where concentrations might exceed threshold levels.

Based on several studies, EPA concluded that EDB is a carcinogen in rats and mice when administered orally or by inhalation. In animal tests, oral administration has caused gastric carcinomas, and inhalation has caused tumors in the spleen, adrenals, and mammary gland (U.S. EPA, 1980). Also, evidence exists indicating that EDB and disulfiram (a widely used alcohol-deterrent drug) act synergistically in causing tumors of many organs of rats (U.S. EPA, 1980; NIOSH, 1978a). EPA also concluded that EDB is a mutagen in test systems and that it causes adverse reproductive effects in the bull, rat, and hen (U.S. EPA, 1980). A quantitative risk assessment is presented in Section 2.2.9.

### 2.2.6 Ecological Effects

The concentration of EDB required to kill half of an aquatic test population within 96 hr was estimated at 10 to 100 ppm (NIOSH, 1978), and the 48-hr median lethal dose for bluegill and largemouth bass was 18 and 15 ppm, respectively.

We have found no data regarding bioaccumulation and biodegradation of EDB in the environment; however, its chemical and biological reactivity may be sufficient to prevent serious accumulations under light loading conditions.

### 2.2.7 Pollution Control Technology

If necessary, EDB emissions could be tightly controlled in a manner similar to those used for vinyl bromide or for DBCP. (Please refer to those sections.)

### 2.2.8 Analytical Methods

Pellizzari et al. (1978b) measured EDB in ambient air by initially collecting the vapors on Tenax GC and ultimately introducing them into a gas chromatographic column (high-resolution glass capillary) followed by a mass spectrometer. The estimated detection limit was 0.530 ng/m$^3$ (0.07 ppt).

Abdel-Kadel et al. (1979) reported a method for determining EDB in treated soil by distilling the EDB from an aqueous slurry of soil into a mixture of acetone and isooctane. The EDB is then decomposed to hydrogen bromide, which is injected into an indium-lined cavity of a molecular emission cavity analysis instrument, where quantification depends on the intensity of the indium bromide emission at the 376-nm wavelength.

### 2.2.9 Carcinogenic Risk Assessment

#### Airborne Exposure

In Appendix D, we computed from others' data that cancer incidence from airborne EDB exposures would be 20, 15, and 7 per year in c. 1975, 1980, and 2000, respectively, with nearly 80% attributable to persons residing near gasoline service stations. Because of the uncertainties involved in this estimation, the major ones being the carcinogenic potency of EDB in humans and the population exposure estimates, this estimate of cancer incidence could be off by up to several orders of magnitude.

Table 2.2-4 indicates that a small number of warehouse workers experience a high exposure rate and consequently may be at a relatively high risk of contracting cancer, if EDB were carcinogenic to humans.

#### Dietary Exposure

EPA estimated that the lifetime carcinogenic risk to the general public from dietary EDB exposures resulting from fumigations was $3.2 \times 10^{-4}$ cancers/person (Table 2.2-5). Assuming a 70-year lifetime and a U.S. population of $220 \times 10^{6}$, we translate this probability into approximately 1000 cancers per year. Of this number, 647 would be attributable to quarantine fumigation of citrus and tropical fruit, 175 to soil fumigation, 159 to spot fumigation of wheat milling machinery, and 8 to wheat fumigation. EPA is proposing to cancel all of these applications except soil fumigation, which may continue under the conditions that registrants determine if groundwater has been contaminated by soil fumigation and that registrants verify that EDB residues on crops grown in EDB-treated soil do not exceed the detection limit of 1 ppb (U.S. EPA, 1980). The carcinogenic risk estimation for soil fumigation assumes that EDB crop residues are at this level (1 ppb), though they could be lower.

### 2.2.10 Implications for EPA

The estimated carcinogenic risk from non-occupational atmospheric EDB exposures is relatively low compared to the estimated risk from dietary exposures. However, as is discussed in the previous section, EPA proposes to reduce the potential risk from dietary exposures by banning some applications. To further reduce the risk to the public, if necessary, EPA could

Table 2.2-4. Cancer Risk Due to Occupational Inhalation of EDB

| Exposed Group | Range of Exposure (mg/kg/day) | Lifetime Probability Estimates (Cancers/person) | No. of Workers Exposed |
|---|---|---|---|
| Soil injection farmer applicator | $1.5 \times 10^{-5} - 2.8 \times 10^{-3}$ | $1.8 \times 10^{-5} - 3.2 \times 10^{-3}$ | 13,200 |
| Fruit fumigation[3] | | | |
| station corridor | $3.5 \times 10^{-3} - 1.2 \times 10^{-2}$ | $4.1 \times 10^{-3} - 1.3 \times 10^{-2}$ | 11[1] |
| station outdoor operator | $7.8 \times 10^{-3} - 10.0 \times 10^{-3}$ | $9.1 \times 10^{-3} - 1.2 \times 10^{-2}$ | 10 |
| trucker/station personnel | $6.2 \times 10^{-4} - 3.2 \times 10^{-3}$ | $7.2 \times 10^{-4} - 3.8 \times 10^{-3}$ | 10 |
| Warehouse[3] | | | |
| Indoor laborer | 0.4 | 0.4 | 4-10(2) |
| Outdoor laborer | 0.1 | 0.1 | 4-10 |
| Stickman | 0.2 | 0.2 | 4-10 |
| Spot fumigation | | | |
| Applicator | $6.6 \times 10^{-3} - 9.1 \times 10^{-2}$ | $7.7 \times 10^{-3} - 0.10$ | 2400-6000 |
| Millworker | $1.5 \times 10^{-2} - 1.7 \times 10^{-2}$ | $1.7 \times 10^{-2} - 2.0 \times 10^{-2}$ | 16,000 |

1 Assumed that 31 federal and state employees are evenly distributed.
2 Per warehouse. Seasonal variation. Assumed that 12-30 laborers per warehouse are evenly distributed.
3 Figures are for Florida only. No data are available as to exposures in Texas or Hawaii.

Source: U.S. EPA, 1980, p. 65

Note: For use in the risk assessment for airborne exposures in Appendix D, Winzler and Kelly calculated the average of the carcinogenic risk factors in this table by dividing the "lifetime probability estimates" by the corresponding "range of exposure" and averaging the values:

$$(1.8/1.5 + 3.2/2.8 \ . \ . \ . \ 1.7/1.5 + 2.0/1.7)/15 = 1.13 \text{ cancers/person per mg/kg-day.}$$

Dividing this factor by the 71.3-yr lifetime assumed by EPA, we get a factor of 0.016 cancer/person-yr per mg/kg-day, which is used in Appendix D.

### Table 2.2-5. Estimates of the Cancer Risk Due to "Probable EDB Dietary Burden"

| Source | EDB Dietary Burden (mg/kg/day) | Lifetime Probability of EDB-Induced Cancer |
|---|---|---|
| Soil Fumigation | $2.6 \times 10^{-7}$[a] | $5.6 \times 10^{-5}$[a] |
| Grain Fumigation (wheat) | $1.8 \times 10^{-7}$ | $2.6 \times 10^{-6}$ |
| Spot Fumigation (wheat) | $3.2 \times 10^{-6}$ | $5.1 \times 10^{-5}$ |
| Quarantine Fumigation: | | |
| Citrus | $1.1 \times 10^{-5}$ | $1.8 \times 10^{-4}$ |
| Tropical fruit | $1.7 \times 10^{-6}$ | $2.7 \times 10^{-5}$ |
| Total | $1.6 \times 10^{-5}$ | $3.2 \times 10^{-4}$ |

Source: U.S. EPA, 1980, p. 60 and 62.

[a] Upper limit. Assumes that EDB concentration in food is 1 ppb, the limit of detection, although residues have not been detected.

control industrial emissions under Section 112 of the Clean Air Act (NESHAP), as it did vinyl chloride. This matter is under consideration at EPA, but will likely not receive great attention for at least a few years (Shell, 1980). Table 2.2-3 indicates that the greatest non-occupational exposures occur to persons residing near service stations. Mara and Lee (1978, p. 32) discussed monitoring data suggesting that the vapor-recovery systems employed on gasoline pumps at service stations in Los Angeles, California substantially reduced EDB emissions from this source.

From the viewpoint of environmental protection, the changes in the EDB market associated with the declining usage of leaded gasoline would appear to have been positive. Reduced consumption of EDB in gasoline should tend to reduce exposures to EDB, unless plants are not maintained as they would be under more favorable market conditions, resulting in increased emissions.

## 2.3 Methyl Bromide

### 2.3.1 Introduction

Methyl bromide (bromomethane) is used mainly as a fumigant. Because of its volatility, it is used as a space fumigant to a much greater extent than is ethylene dibromide. It is used in grain elevators, grain mills, ships, greenhouses, soil, and in buildings for termite control (Fowler, 1980). When used as a soil fumigant, it is injected into the soil or to the surface under tarps (NAS, 1978, p. 81). Target organisms include microorganisms (viruses, bacteria and bacterial spores, and fungi), invertebrate animals (including insects, cockroaches, mites, nematode worms, moth larvae, ticks), rodents, and weeds (Fowler, 1980).

The distribution of domestically produced methyl bromide is shown in Table 2.3-1.

Methyl bromide is a colorless, nonflammable gas above 3.5°C. Table 2.3-2 shows some of the properties of methyl bromide.

### 2.3.2 Production and Consumption

Reported domestic production of methyl bromide is shown in Table 2.3-3. Table 2.3-4 lists the producers, plant locations, and annual production capacities as reported in 1977. From Table 2.3-1, we may assume that roughly 75% of domestic production is consumed in the U.S. The amount of methyl bromide used on tobacco was reported to be $6.6 \times 10^6$ lb in 1976 (Eichers et al., 1978). This number does not include usage on fruits and vegetables or for space fumigation. In 1979, $8.4 \times 10^6$ lb were used in California (Calif. Dept. Food & Agr., 1980).

Our research has not detected any activities that would substantially alter the demand for methyl bromide, except for

Table 2.3-1. Distribution of Domestic Methyl Bromide Production

| Use | Percent |
|---|---|
| Soil Fumigant | 55 |
| Space Fumigant | 15 |
| Other | 5 |
| Exports | 25 |
| | 100 |

---

Source: CMR, 1978

## Table 2.3-2. Chemical and Physical Properties of Methyl Bromide

| | |
|---|---|
| Chemical Formula | $CH_3Br$ |
| Synonyms | Bromomethane |
| CAS Registry Number | 74-83-9 |
| NIOSH RTECS Number | PA 4900000 |
| Molecular Weight | 94.95 |
| Boiling Point @ 760 torr | 3.56°C |
| Freezing Point @ 760 torr | -94.07°C |
| Specific Gravity | 1.737 @ -10°C |
| Vapor pressure @ 20°C | 26 psia<br>1250 mmHg[a]<br>1420 mmHg[b] |
| Vapor Density | 3.27[c] |
| Auto Ignition Temperature | 537°C |
| Flash Point | None[a] |
| Odor | Sweet, chloroform-like |
| Color | Colorless |
| Solubility | Miscible in acetone, carbon tetrachloride, benzene, ethyl ether, n-heptane, ethanol<br><1000 ppm (0.1 gm/100 gm) in water |
| Conversion @ 20°C | 1 $mg/m^3$ = 253 ppt |

---

Source: Davis et al., 1977, except as noted otherwise.

[a] Source: Hawley, 1977.

[b] Source: Merck, 1976.

[c] Source: Verschueren, 1977.

Table 2.3-3. Domestic Production of Methyl Bromide

| Year | $10^6$ lb |
|---|---|
| 1969 | 20.0 |
| 1970 | 21.0 |
| 1971 | a |
| 1972 | 24.6 |
| 1973 | 29.6 |
| 1974 | 30.4 |
| 1975 | 36.0 |
| 1976 | 35.8 |
| 1977 | 34.7 |
| 1978 | 36[b] |
| 1980 | 38[c] |
| 1982 forecast | 45[b] |
| 1985 forecast | 49[c] |

---

Source: Fowler and Mahan, 1980, except as noted otherwise.

[a] Withheld to avoid disclosure.

[b] Source: CMR, 1978.

[c] Source: CMR, 1981.

Table 2.3-4. Producers and Capacities for Methyl Bromide[a]

| Producer | Plant Location | Production Capacity ($10^6$ lb/yr) | |
|---|---|---|---|
| Dow Chemical Co. | Midland, MI | 21 | 25[c] |
| Great Lakes Chemical Corp. | El Dorado, AR | 33 | 35[c] |
| Velsicol Chemical Corp. | St. Louis, MI | 5[b] | |

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[a] Some capacities can be used to make other bromine compounds.

[b] Scheduled to terminate by Sept. 1978. Confirmed by Whitney (1981) that the entire plant is being demolished and that operations closed in Sept. 1978, despite the report by U.S. ITC (1980) that Velsicol produced methyl bromide in 1979 and despite the reporting by Velsicol to the Bureau of Mines that Velsicol produced methyl bromide in 1980 (Lyday, 1981).

Source: CMR, 1978, except as noted otherwise.

[c] Source: SRI, 1980.

perhaps regulations under the Federal Insecticide, Fungicide and Rodenticide Act. Methyl bromide will be reviewed by EPA to determine if any pesticide registrations should be cancelled to protect human health or the environment (U.S. EPA, 1980); however, this review will not be complete for at least another year or two (Johnson, 1980).

Because methyl bromide might be substituted for EDB in some pesticide applications, cancellation of EDB registrations could drive up the demand for methyl bromide, although this would likely be very minor for the following reasons. EPA is proposing to cancel EDB registrations for use on fumigation of stored grains and spot fumigation of grain-milling machinery, fumigation of felled logs, and fumigation of harvested citrus, tropical fruits, and vegetables. Methyl bromide is a viable substitute for EDB's use on grains and mills, but EPA estimates that only 465,000 lb/yr of EDB are used for this purpose. The use of EDB on felled logs and harvested fruits and vegetables is also relatively minor, and methyl bromide is not considered to be an alternative for these applications. Nearly all of the pesticidal use of EDB is for pre-plant soil fumigation, and EPA is not proposing to cancel registrations for this purpose (U.S. EPA, 1980).

Although a device called the zapper, which kills weeds and pests with microwave energy, was marketed in 1973 and reported to offer competition with methyl bromide (Chemical Engineering, 20 Jul 1973, p. 55), production of methyl bromide has increased substantially since that year.

In addition to the slow, steady growth experienced by methyl bromide, its use as a methylating agent in chemical syntheses is reportedly expanding significantly, although this use was still relatively small in 1978. Growth through 1982 was forecasted to continue at the 1967 to 1977 annual rate of 4 to 5 percent (CMR, 1978). A more recent report put the 1971 to 1980 growth rate at 6.1 percent per year and future growth at 5 percent per year through 1985 (CMR, 1981).

### 2.3.3 Emissions and Atmospheric Concentrations

Methyl bromide can be produced by the bromination (with liquid bromine or a bromide salt) of methanol in the presence of sulfuric acid. The methyl bromide is expelled from the reaction mixture with heat, and the methyl bromide vapors are condensed and collected. Methyl bromide's volatility increases the opportunities for its escape to the atmosphere during production and handling. Brown et al. (1975a) estimated that 1% of production escapes at the plant site, but NAS (1978) put this rate at 0.6%. An excess of sulfuric acid or heat results in the formation of dimethyl sulfate (Davis et al., 1977).

During methybromide production, an excess of sulfuric acid or heat results in the formation of dimethyl sulfate (Davis et al., 1977), a confirmed animal carcinogen. Dimethyl sulfate's low volatility and high susceptibility to hydrolysis will ensure a short lifetime in the environment (IARC, 1974). Thus, dimethyl sulfate should not pose a significant airborne carcinogen hazard. Moreover, dimethyl sulfate is likely produced in very small amounts, if at all, as a contaminant, as producers strive to avoid product contamination and waste of materials (sulfate and heat).

The greatest anthropogenic emissions of methyl bromide occur during its use. It has been estimated that 25% of industrially produced methyl bromide is released to the atmosphere, mostly during fumigation operations, (Wofsy et al., 1975; Singh et al., 1977a), but that 75 to 95% of the methyl bromide in the atmosphere is likely derived naturally from the oceans (Wofsy et al., 1975). NAS (1978) put total emissions to the environment (mostly air) at 71% of production, which would amount to 25 x $10^6$ lb methyl bromide from the 1978 level of production. NAS (1978, p. 81, 82) also reported that little of the methyl bromide applied to soil is emitted during the application process, but that 30% of that used in space fumigation may be emitted to the atmosphere while the rest decomposes to inorganic bromides and methylated derivatives of organic compounds.

Harch and Rasmussen (1977) reported that methyl bromide is emitted by automobiles burning leaded gasoline, where ethylene dibromide (EDB) is the suspected source. Table 2.3-5 shows that the highest concentration of methyl bromide in the exhaust of four automobiles tested was 55,000 ppt. We roughly estimated the fraction of the EDB contained in the gasoline that would be converted to methyl bromide at 4 x $10^{-5}$ g MeB/g EDB[1]. At this rate, assuming that 185 x $10^6$ lb/yr of EDB are currently consumed in motor vehicles, roughly 37,000 lb/yr of methyl bromide would be emitted from motor vehicles using leaded fuel containing EDB, a relatively small and dispersed source.

We have found no indication that methyl bromide is discharged to water in substantial quantities. None was reported in the spent brine at a bromine production facility (Pellizzari et al., 1978a) or in fresh water or drinking water (NAS, 1978). During production, methyl bromide is expelled from the reaction mixture during a distillation process, which should result in a very low concentration in the wastewater. NAS (1978) did not report any methyl bromide in precipitation, surface water, or finished drinking water, as it did for other brominated and chlorinated methanes.

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[1] We calculated that a 250 $in^3$, 6-cylinder engine running at 3000 rpm would exhaust 5,520 l/min; assumed that at 3000 rpm, 55 mph, and 20 mpg, the car would burn about 15 gal gasoline in roughly 6 hr; assumed that gasoline contains 0.65 g Br/gal (see EDB section); and assumed that the exhaust temperature when analyzed was 120°C.

Table 2.3-5. Concentrations of Methyl Bromide in Urban Air and Automobile Exhaust

| Date | Sample Description | Methyl Bromide (ppt) |
|---|---|---|
| 9/13/76 | Street corner, moderate traffic, 10 mph wind | <10 |
| 9/13/76 | Same, heavy traffic | <10 |
| 10/1/76 | Automobile exhaust, leaded fuel, 1972 Rambler | 55,000 |
| 10/1/76 | Auto exhaust, non-leaded fuel, catalytic converter, 1976 Ford Pinto | <1,000 |
| 11/6/76 | Street corner, light traffic, calm early morning with heavy inversion | 220 |
| 11/6/76 | Same, heavy traffic, slight breeze | 150 |
| 11/16/76 | Street corner, light traffic, 5 mph wind | <10 |
| 11/16/76 | Same, heavy traffic | 185 |
| 11/16/76 | Auto exhaust, leaded fuel, 1972 Rambler | 18,000 |
| 11/16/76 | Auto exhaust, non-leaded fuel, catalytic converter, 1975 Ford Pinto | 1,300 |

Source: Harsch and Rasmussen (1977).

Pellizzari et al. (1978a) conducted an extensive investigation into the contamination of the environment by brominated compounds surrounding five bromine-production facilities in Arkansas: Arkansas Chemicals, Inc., Great Lakes Chemical Corp., and Velsicol Chemical Corp. near El Dorado, and Dow Chemical Co. and Ethyl Corp. near Magnolia. Of these, only the Great Lakes and Velsicol facilities near El Dorado produced methyl bromide (Table 2.3-4). Traces of methyl bromide were detected near Velsicol in two samples and near Ethyl in one sample. It was also detected near Arkansas Chemicals, and the detection limit was reported to be 120 $\mu g/m^3$ (30,360 ppt) (Pellizarri et al., 1978a). However, Pellizarri et al. (1978b) also reported a "lower limit of measurement" for methyl bromide of 500 ppt, and Singh et al. (1977a) reported a detection limit of 30 ppt. Therefore, we conclude that the stated detection limit of 120 $\mu g/m^3$ in Pellizzari et al. (1978a) should have read 120 $ng/m^3$, which is equivalent to 30 ppt. This would be consistent with the expression of all other concentrations for volatile brominated organics in $ng/m^3$ in that report. Considering that methyl bromide is found as a natural component of the atmosphere in the 30 ppt range (Singh et al., 1977a, 1977b), we conclude that it was not found in elevated concentrations near any of the facilities.

Assuming that the current methyl bromide production rate is $39 \times 10^6$ lb/yr; that production is at 72% of capacity (see Table 2.3-3 and 2.3-4) and that, therefore, production at Great Lakes Chemical Corp. near El Dorado, Arkansas would be $24 \times 10^6$ lb/yr; that emissions are 0.6% of production; and that plant downtime is 15 d/yr, a 10-min ground level concentration 500 m downwind from the plant of 212 $\mu g/m^3$ (54 ppb) was calculated using the method described in Appendix B. At 100 m, the calculated concentration is 148 ppb. However, using this same methodology, we calculated a concentration of 160 ppb ethylene dibromide (EDB) 100 m downwind of this facility, whereas Mara and Lee (1978) assumed an annual average of 5 ppb based on monitoring data around Dow's EDB facility at Magnolia, Arkansas. The 5-ppb level should be more representative of the annual average rather than the 148 ppb 10-min average. However, a wide range of uncertainty in these estimates exists because of poorly known emission factors and scanty monitoring data.

The oceans are thought to be the major sources of atmospheric methyl bromide (Singh et al., 1977a, 1977b; Wofsy et al., 1975). It has been found in seawater at concentrations of 2.5 ppb (Lovelock, 1975) and 0.14 ppb (Singh et al., 1977a), measured as the concentration in inert gas that is in equilibrium with the seawater. Theiler et al. (1978) demonstrated the formation of dibromomethane, bromoform, and 1-pentyl bromide from a marine red algal enzyme (bromoperoxidase) incubated with hydrogen peroxide, bromide ion, and 3-oxooctanoic acid. Other systems may generate methyl bromide.

Considering that 60 to 70% of domestic production is used in soil and space fumigation (Table 2.3-1), that much would be available for distribution to the air, soil, and water, though it is known that much is decomposed in reactions with organic materials (NAS, 1978).

Davis et al. (1977) stated that because so much methyl bromide was released to the environment during its use as a fumigant, emissions from waste disposal was likely to be insignificant by comparison, especially considering that it is a moderately expensive industrial chemical.

Methyl bromide was detected, but not quantified, in the air space of acrylic and modacrylic carpet and fabric by direct insertion mass spectrometry. No indication of the magnitude of the concentration was available, nor was an explanation of the occurrence of methyl bromide provided (Finkel et al., 1979).

Table 2.3-6 summarizes the available data on atmospheric concentrations of some non-fluorinated halomethanes, showing that methyl bromide is present in low concentrations compared to some. The source of elevated urban concentrations of methyl bromide may be automobiles burning leaded gasoline (Table 2.3-5).

### 2.3.4 Environmental Fate

#### Water

Because of its high volatility, methyl bromide would have a great tendency to evaporate from water. Data on rates of hydrolysis are conflicting. Davis et al. (1977) stated that it hydrolyzes slowly to methanol and HBr, the rate of hydrolysis being lower in neutral or acid waters (i.e., fresh waters) than basic water (i.e., seawater). The half-life for methyl bromide in aqueous solution at 25°C and pH 4 to 10 has been estimated to be 480 days (NAS, 1978, p. 39). However, Brown et al. (1975a) stated that methyl bromide hydrolyzes fairly rapidly (half-life = 15 d). NAS (1978) stated that, in fumigation chambers, much of the methyl bromide decomposes to inorganic bromides and methylated derivates of organic compounds. Such reactions may also occur in water. Quantitative data on the chemical and biological degradation of methyl bromide in water is very deficient.

#### Soil

During soil fumigation methyl bromide is injected into the soil or under a tarp lying on the ground. It has been known to diffuse downward in the soil from an injection point of 3 to 5 ft to 9 to 12 ft below the surface (Davis et al., 1977), perhaps eventually reaching groundwater. Its high volatility would encourage its diffusion from the soil to the atmosphere, but this tendency would be counteracted by its high vapor density with respect to air (3.27). Methyl bromide has been detected in soil 14 d after injection, but it is known to degrade in soil, although the mechanism and rate of degradation has not been studied (Davis et al., 1977).

Table 2.3-6. Summary of Atmospheric Concentrations of Nonfluorinated Halomethanes (ppt)*

| Compound | Continental Background | Marine Background | Urban Range |
|---|---|---|---|
| Methyl Bromide<br>($CH_3Br$) | 15 ± 10<br>0.5 to 1.0 | 93 ± 100 | 108 ± 138<br>10 to 220 |
| Methyl Chloride<br>($CH_3Cl$) | 569 ± 42<br>530 ± 30<br>587 ± 102<br>713 ± 51<br>1,040 ± 399<br>690 ± 390 | 1,260 ± 434<br>1,140 ± 400 | 834 ± 40 |
| Methylene Chloride<br>($CH_2Cl_2$) | 36 ± 11 | 35 ± 19 | 20 to 144 |
| Chloroform | 9 ± 3<br>11 ± 5<br>25 ± 18 | 40 ± 38<br>27 ± 8 | 102 ± 102<br>10 to 15,000<br>6 to 3,000 |
| Carbon Tetrachloride<br>($CCl_4$) | 20 ± 10<br>122 ± 13<br>133 ± 10<br>116 ± 8<br>120 ± 15 | 128 ± 4<br>128 ± 16<br>111 ± 11 | 134 ± 20<br>120 to 18,000<br>1,400<br>120 to 1,500 |
| Methyl Iodide<br>($CH_3I$) | 9 ± 5 | 7 ± 7<br>1 to 11 | 24 ± 20<br>1 to 3,800 |

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*The ± indicates typically one standard deviation.

Multiple entries indicate multiple sources of data, and the data were not consistently reported in the same format.

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Source: NAS, 1978.

## Air

Methyl bromide is thought to decompose in the troposphere (lower atmosphere, 0 to 10 km), through hydroxyl radical (OH) attack, with ultraviolet photolysis increasing in importance with altitude and being dominant at 25 km. The atmospheric lifetime of methyl bromide is estimated to be somewhat less than 0.4 to 0.9 years, and the major decomposition products are presumed to be Br, CO, and $CO_2$ (NAS, 1978). Some form or forms of inorganic bromine would also be expected.

Wofsy et al. (1975) considered the potential for atmospheric bromine to decompose (recombine) ozone in the stratosphere (10 to 50 km), suggesting that bromine may be a more efficient catalyst for ozone recombination than chlorine. They forecasted reductions in the estimated 1980 stratospheric ozone concentration by year 1990 ranging from 0.2 to 4%, depending on model assumptions and on the assumed annual growth rate (7 to 15%) in the pesticidal use of methyl bromide, which was confirmed by Yung et al. (1980). This compares to a forecasted 5% decline in stratospheric ozone by 1990 from just two chlorofluoromethanes: F-11 and F-12 (NAS, 1979a, p. 176). Neither of two recent studies of stratospheric ozone depletion by halocarbons (NAS, 1979a and 1979b) discuss bromine as a contributing factor, probably because one- and two-carbon chlorofluorinated and chlorinated compounds are produced and released in much greater quantities than are brominated compounds. Nevertheless, the results of Wofsy et al. (1975) and, more recently, Yung et al. (1980), indicate that bromine may pose a significant threat to stratospheric ozone and should be addressed by those involved in evaluating the effects of man's activities on stratospheric ozone.

## Food

NAS (1978) stated that methyl bromide is lost rapidly from fumigated foods and that, because of its high volatility and reactivity with organic compounds, it reaches consumers in insignificant amounts. On samples of longhorn cheese, methyl bromide residues decreased to 1 to 2 ppm within 7 d of fumigation, and roughly one-third of the methyl bromide initially contained in the cheese was converted to inorganic bromides. It was also reported that no methyl bromide was found in asparagus, avocados, peppers, and tomatoes after fumigation for 2 hr at 32 mg/l, and only trace amounts in hard-wheat flour 9 d after being fumigated with 36.6 mg/l (NAS, 1978). However, Davis et al. (1977) reported that methyl bromide was absorbed by peanuts and grain and that cows fed fumigated grain produced milk with bromide concentrations proportional to the amount of fumigated grain in their diet. Diets containing up to 43 ppm inorganic bromide (originating from methyl bromide residues) resulted in the milk containing 10 to 20 ppm bromide, though methyl bromide detection in the milk was not reported. Methyl bromide was reportedly found in milled wheat products made from wheat fumigated prior to milling. Concentrations up to 111 ppm bromide were reported for fumigation with 3 lb methyl bromide per 1000 $ft^3$ of space (Davis et al., 1977).

Davis et al. (1977) stated that methyl bromide is widely used for controlling pests in the food industries, but no information was found on how much, if any, is contained in food that is offered for human or animal consumption.

### 2.3.5 Health Effects

Methyl bromide can cause a variety of symptoms, including headache, visual disturbance, vertigo, nausea and vomiting, malaise, hand tremor, convulsions, dyspnea, eye and skin irritation, and vesiculation (NIOSH/OSHA, 1978). Methyl bromide can be absorbed into the body through the lungs, gut, and, perhaps, skin, and it is rapidly degraded and excreted (NAS, 1978). Its mechanism of action is uncertain, but methylation of cellular components, perhaps sulhydryl groups of enzymes, is possible (Davis et al., 1977).

Methyl bromide's permissible occupational exposure limit (8-hr time-weighted average) is 20 ppm, the Threshold Limit Value (Am. Conf. of Governmental Industrial Hygienists) is 15 ppm, and the level considered to be immediately dangerous to life or health is 2000 ppm (NIOSH/OSHA, 1798). Because measured environmental levels are roughly $6 \times 10^{-6}$ times the established occupational limit, no concern exists over non-carcinogenic or non-teratogenic effects, except in the workplace and in accidental-spill situations.

NIOSH's Registry of Toxic Effects of Chemical Substances subfiles contain no indication that methyl bromide is either tumorigenic, mutagenic, or teratogenic (NIOSH, 1979). However, two recent reports (Mortelmans and Shepherd, 1980; Rounds, 1980) were reviewed by an EPA toxicologist, who concluded that methyl bromide caused mitotic recombination in the yeast Saccharomyces cerevisiae and, possibly, sister chromatid exchanges in the Chinese hamster (Schneider, 1980). Brown et al. (1975a) reported that a test on dogs (35 to 150 mg/kg orally for 1 yr) was negative for carcinogenicity. We know of no other carcinogenicity tests for methyl bromide.

### 2.3.6 Ecological Effects

The concentration of methyl bromide required to kill half of the aquatic test organisms during a 96-hr bioassay is considered to be greater than 1000 ppm (NIOSH, 1978). In a review, Brown et al. (1975a) stated that methyl bromide is reported to be toxic to various bacteria and fungi, although no toxic levels were specified in the original literature.

Methyl bromide's volatility and its apparent propensity to degrade in biological systems (see Environmental Fate) suggest that it would not cause significant ecological damage in low concentrations, although we have found no indication that this has been studied. In monitoring studies, Pellizarri et al. (1978a) did not find methyl bromide in elevated concentrations in the environment surrounding production facilities in Arkansas.

Bromide ion is expected as a breakdown product in water and soil, possibly accumulating in soil and some plants, although we have found no data on this subject.

### 2.3.7 Pollution Control Technology

We found no discussion of pollution controls in the literature. Substantial workplace controls are likely required to meet the 20-ppm occupational standard, as for vinyl bromide. Control of airborne emissions could be achieved to very low levels if desirable, as for dibromochloropropane (Section 2.8.7).

### 2.3.8 Analytical Methods

Pellizari et al. (1978b) tested for methyl bromide in air using the same GC-MS procedures as for vinyl bromide, with a detection limit of 11 ng/$m^3$ (2.8 ppt) at 15.5°C. The GC-MS procedure used for ethylene dibromide was not suitable for methyl bromide. Others have used gas chromatography with electron capture detector (GC-EC) to detect methyl bromide down to 30 ppt (Sing et al., 1977a). Methyl bromide in water has been measured by purging it from solution with inert gas, then testing the gas by GC-EC (Lovelock, 1975; Sing et al., 1977a, 1977b).

### 2.3.9 Implications for EPA

Our assessment has not identified any substantial environmental hazards associated with the production and use of methyl bromide to date; however, the lack of carcinogenic potency data (if it is carcinogenic) and of an accurate point-source emissions inventory prevents a realistic risk assessment. The lack of carcinogenicity and food-residue data may hamper EPA's planned review of methyl bromide under its Rebuttable Presumption Against Registration (RPAR) process. Another area of concern that should receive further attention is methyl bromide's potential for destroying stratospheric ozone. Two analyses have suggested that this effect could become significant as the dispersive use of methyl bromide increases, but no further attention has been given to this in recent major assessments on stratospheric ozone.

If a reduction in methyl bromide emissions and exposures were desirable, the most likely avenue for regulation would be Section 112 of the Clean Air Act (National Emission Standards for Hazardous Air Pollutants), as for vinyl chloride, and the RPAR process under the Federal Insecticide, Fungicide, and Rodenticide Act, administered by the Office of Pesticide Programs of EPA, as for EDB.

## 2.4 Flame Retardants[1]

### 2.4.1 Introduction

Because of federal fire-safety regulations, combustible materials are often treated with or manufactured with flame-retardant chemicals, also commonly known as fire retardants. Over half of the domestic production of flame retardants is used in carpets, rugs, and their underlays (Sanders, 1978). The bromine-based fire retardants comprise roughly 5% of the total fire retardant market. Other fire retardants are based on aluminum, antimony, phosphorus, chlorine, boron, and other minerals (Chem. & Engr. News, 17 Nov. 1980, p. 26).

McGeehan and Maddock (1976) reviewed the use of flame retardants in textiles, but their report is of little value to the present one because of the lack of detailed chemical-specific information. Appendix C lists nearly 50 brominated compounds reportedly used as flame retardants, but the demand for all but a relatively few is likely very limited.

### 2.4.2 Production and Use

The Fire Retardant Chemicals Association (Westport, Conn.) provided much information on the fire retardant chemicals industry. The association has tried to collect production data from manufacturers, but some key firms have not cooperated to date for fear of exposing proprietary information. Therefore, the association feels that no accurate industry-wide production data have been collected for any type of fire retardant, although it is optimistic that greater participation will be experienced within the next few years.

The association estimates the annual domestic production of bromine-based fire retardants at between 30 x $10^6$ lb and 50 x $10^6$ lb, with the distribution shown in Table 2.4-1. Such very rough estimates must be tempered by reports that 15 x $10^6$ lb of additional tetrabromophthalic anhydride capacity is being constructed by Velsicol at El Dorado, Arkansas (10 x $10^6$ lb per year) (Chem. Week, 31 Jan. 1979, p. 21) and by Saytech at Sayreville, N.J. (5 x $10^6$ lb per year) (Chem. Mark. Rep., 5 Feb 1979, p. 7), and that Great Lakes Chemical has doubled its production capacity for decabromodiphenyl oxide and will expand its capacity for tetrabromobisphenol-A (Plastics World, Aug. 1979, p. 11).

A recent proprietary report estimated 1980 demand at 32 x $10^6$ lb (Chem. Engr. News, 17 Nov. 1980, p. 26). Modern Plastics (Sept. 1980, p. 45) estimated that the use of flame retardants in plastics alone amounted to 34 x $10^6$ lb in 1980; therefore, the total usage would be greater than this. Chemical Age (5 May 1978, p. 11) forecasted a demand of 49 x $10^6$ lb in 1981 for brominated bisphenol A and brominated hydrocarbon flame retardants. Because imports of brominated chemicals are small (Table 2.1-4) these usage figures can be assumed to represent consumption of domestically produced flame retardants.

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[1] Also see separate sections on "Tris," polybrominated biphenyls, and vinyl bromide.

Table 2.4-1. U.S. Production of Flame-Retardant Chemicals

| Chemical | Uses | Production ($10^6$ lb/y) |
|---|---|---|
| Tetrabromobisphenol A | epoxy resins | 11-14 |
| Decabromodiphenyl oxide | polystyrene | 5-10 |
| Others | | 10-20 (none over 5) |
| Dibromoneopentyl glycol | [1] | |
| Pentabromodiphenyl oxide | [1] | |
| Tetrabromophthalic anhydride | [1] | |
| Proprietary formulas | | |
| Total | | 26-44 |

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Source: Fire Retardant Chemicals Association, Westport, Conn.

[1] See Appendix C.

The various estimates presented above are very different from the Bureau of Mines' estimated 1979 demand of 111 x $10^6$ lb bromine for fire retardants, which is similar to another estimate of 118 x $10^6$ lb (CMR, 1979). The Fire Retardant Chemicals Association felt that any estimated production rate over 50 x $10^6$ lb/yr was excessively high. But the higher estimates likely include other chemicals, such as those used in fire extinguishers, not included in the lower estimates.

According to the Fire Retardant Chemicals Association, imports are not expected to significantly penetrate the domestic bromine-based fire-retardant market. Because brominated chemicals are heavy, their transportation costs are high, making competition difficult for importers. Imports of bromine compounds are low overall, and no importation of bromine-based fire retardants has been reported (Table 2.1-4).

The Fire Retardant Chemicals Association indicated that most U.S. exports of bromine-based fire retardants are to the far east, which is somewhat closer to Israel (the world's second largest bromine producer) than to U.S. production facilities. This distance disadvantage coupled with the agressive bromine-product export policies of Israel could result in a loss of some U.S. export business.

Fire-safety regulations, such as the Fire Prevention and Control Act and the Flammable Fabrics Act, provide an impetus for the use of fire retardants, ensuring a steady growth in their demand. However, we are aware of no further developments that will cause a large quantum increase in demand or in the rate of increase in demand of bromine-based fire retardants. A recent proprietary report forecasted an annual increase in demand of bromine-based fire retardants of 11.4 percent between 1980 and 1985, the highest growth rate for any type of fire retardant. However, the Fire Retardant Chemicals Association favored a growth rate of 4 to 5% annually for bromine-based fire-retardants. In between these two predictions is that stated by SRI (1980): 7 to 8%/yr on the average. One producer forecasts an annual growth rate of 12% (Chem. Mark. Rep., 6 July 1981, p. 25).

Vinyl bromide, "Tris," and polybrominated biphenyls are other flame retardants for which more detailed information exists. These materials are discussed in their own sections.

### 2.4.3 Environmental Hazards

The chemical structures and uses of brominated fire retardants are included in Appendix C. Several flame retardants -- including decabromodiphenyl oxide, tetrabromobisphenol A, "Tris," and Firemaster 680 -- have been detected in environmental samples taken near production facilities in southern Arkansas. Decabromodiphenyl oxide had the highest concentration in air (94 $\mu g/m^3$) and in sediment (1g/kg). This situation has created some public concern, and further investigations may be undertaken by the Arkansas Department of Health to determine the magnitude of the exposure to persons residing in nearby communities (Wise, 1981). Exposures could be through the air, water, or food chain.

Another source of exposure to flame retardants is through contact with treated end products. A good example of this type of exposure is the absorption of "Tris" from treated children's sleepwear. This may occur with other non-reactive flame retardants that can be removed from the treated material. This is thought to occur with the chlorinated analog of "Tris" (Chem. & Engr. News, 15 Dec. 1980, p. 6; Hudec et al., 1981).

A third potential cause of exposures to flame retardants is the disposal of treated materials by landfilling or incineration. We have found no studies of the potential for groundwater contamination via the land-based disposal of treated materials like carpets, draperies, clothing, and plastics. To our knowledge, no research has been done on the fate of flame retardants during solid-waste incineration.

Little has been reported on the environmental hazards of most flame retardants. Several are briefly discussed below.

## Tetrabromobisphenol A

As a reactive flame retardant (Considine, 1974) (that is, one that is chemically bonded to the synthetic polymer backbone), tetrabromobisphenol A is unlikely to be leached in significant amounts from treated products because the polymers are very resistent to molecular degradation, leaving production facilities as the greatest source of exposure. With a melting point of 181°C (Considine, 1974), its vapor pressure is low, and it is found in the air as a particulate. It can be sampled on Hi-Vol glass fiber filters, extracted with a solvent, and determined by a combination of gas-liquid chromatography and mass spectrometry with multiple ion detection at a limit of detection of 10 ng/$m^3$ (Pellizzari et al., 1978b). Tetrabromobisphenol A has been detected in air (1.8 μg/$m^3$ max.), soil (over 222 mg/kg max.), sediment (330 mg/kg max.), and human hair (13 μg/$m^3$ max.) near production facilities in southern Arkansas (Pellizzari et al., 1978a).

Tetrabromobisphenol A (CAS No. 79-94-7) was reported to have a fairly high acute toxicity in trout and bluegill; where 96-hr median lethal concentrations were 0.40 mg/l and 0.51 mg/l, respectively, and other toxic symptoms were observed below these levels (U.S. EPA, 1980b, p. 224). This high toxicity combined with a high octanol/water partition coefficient of 30,000 (U.S. EPA, 1980b, p. 175) suggest that discharges to surface waters could be an important consideration.

We have found no data concerning the potential for carcinogenic effects from tetrabromobisphenol A. It is not listed in the Registry of Toxic Effects of Chemical Substances (NIOSH, 1978 and 1979). One study reported no teratogenic effects, but EPA concluded that this study was inadequate (U.S. EPA, 1980b, p. 201).

### Decabromodiphenyl Oxide

Very little information on this flame retardant is available in the literature. It has been found in environmental samples taken near production facilities, the highest level in air being 94 $\mu g/m^3$ and in human hair sampling (Pellizzari et al., 1978a). Aquatic biota sampled downstream of bromine-based chemical plants near El Dorado, Arkansas contained decabromodiphenyl oxide at concentrations much lower than 1 ppm (Erickson et al., 1980). It has been analyzed by the same methods as tetrabromobisphenol A, with a detection limit in air of 20 to 100 $ng/m^3$. It was reported to be teratogenic in rats by oral administration and to be under testing at the National Cancer Institute (NIOSH, 1979).

### Tetrabromophthalic Anhydride

Tetrabromophthalic anhydride is another reactive flame retardant with a melting point of 280°C (Considine, 1974). A manufacturer submitted reports to EPA that this compound was not mutagenic and that its 96-hr median lethal concentration in rainbow trout and bluegills was greater than 10 mg/l (U.S. EPA, 1980b, p. 300). A pilot teratology study that did not demonstrate adverse effects in rats was deemed to be too insensitive by EPA (U.S. EPA, 1980b, p. 186).

### Firemaster 680

FM680 (1,2-bis (2,4,6-tribromophenoxy) ethane) was reported to be non-mutagenic in the Ames test and in a yeast assay, accumulate in the liver and fat of rats exposed by inhalation, be slowly degraded in sewage and soil, be moderately toxic to fish, and concentrate slightly in carp (U.S. EPA, 1980b, p. 294).

We have found no information on the production and consumption levels of FM680. It has been analyzed in environmental samples as for tetrabromobisphenol A, with a detection limit in air of 10 $ng/m^3$. FM680 was measured near Velsicol's facility in southern Arkansas at up to 183 $ng/m^3$ in air and 466 $\mu g/kg$ in sediment (Pellizzari et al., 1978a).

### 2.4.4 Implications for EPA

Because many brominated chemicals are or might be used as flame retardants and because little information is readily available on them, a detailed analysis of each was beyond the scope of this study (but see also the sections on vinyl bromide, "Tris," and polybrominated biphenyls). Further study in this area is needed and is being done by EPA presently.

The Office of Pesticides and Toxic Substances of EPA is presently conducting a study designed to accomplish the following tasks:

1. Analysis of Flame Retardant Industry
2. Identification of Hazardous Flame Retardants
3. Life-Cycle Analysis of Flame Retardants in Fibers
4. Life-Cycle Analysis of Flame Retardants in Plastics
5. Life-Cycle Analysis of Flame Retardants in Paints
6. Life-Cycle Analysis of Flame Retardants in Miscellaneous Uses
7. Conclusions and Recommendations

The study will be used to determine if regulatory action under the Toxic Substances Control Act is warranted. The Project Officer is Dr. William M. Stigliani of the Chemical Control Division (TS-794).

## 2.5 Calcium Bromide

### 2.5.1 Introduction

The demand for calcium bromide has grown tremendously since its introduction as a well-drilling fluid in 1972 (Chemical Engineering, 1 Jan. 1979, p. 41). Since 1976, domestic production increased from nearly zero to over 100 x $10^6$ lb in 1978. This increased demand stems from the oil and gas industry's attempt to increase production (Journal of Commerce, 18 Sept. 1979, p. 1). Completion fluids are used to avoid clogging of the pores when final preparation of the surface of the well bore is conducted.

For use as a solids-free drilling fluid used in the completion of wells, calcium bromide is produced as a 53% (by weight) aqueous solution having a specific gravity of 14.2 lb/gal. Production data for calcium bromide completion fluids are for the solution, not for $CaBr_2$ (Anonymous major producer, December 1980). To convert a given weight of calcium bromide completion fluid to the amount of contained $CaBr_2$ or bromine, multiply by 0.53 or by 0.42, respectively.

### 2.5.2 Production and Consumption

Some inaccuracies and omissions in the recent literature have occurred regarding the domestic production of calcium bromide completion fluids. According to a major producer, the domestic producers and their approximate annual production capacities are shown in Table 2.5-1.

Dow has postponed plans for a capacity addition of 120 x $10^6$ lb/yr at Magnolia, Arkansas until the mid-1980's. Great Lakes is reportedly expanding capacity to 100 x $10^6$ lb/yr (Chem. & Engr. News, 22 Jan. 1979, p. 15). An industry source estimated current domestic production at roughly 130 x $10^6$ lb/yr, of which approximately 10 to 15% is exported.

## Table 2.5-1. Approximate Domestic Production of Calcium Bromide Completion Fluid

| Firm | Location | Calcium Bromide Completion Fluid ($10^6$ lb) | Contained Bromine ($10^6$ lb) |
|---|---|---|---|
| Dow Chemical Co. | Midland, MI | 120 | 50 |
| Great Lakes Chemical Corp. | El Dorado, AR | 80 | 34 |
| Ethyl Corp. | | 60 to 70 | 25 to 29 |
| Velsicol Chemical Corp.[a] | Beaumont TX and El Dorado, AR | 30 | 13 |
| | Total | 295 | 124 |

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Source: Anonymous Major Producer, 1980, except as noted otherwise.

[a] Source: Chem. & Engr. News, 27 Nov. 1978, p. 12.

Demand for calcium bromide completion fluids is experiencing a strong growth rate of roughly 15% per year, but the industry is currently not producing up to capacity, according to a major producer. Dow Chemical Co. is planning a 120 x $10^6$ lb/yr expansion of production capacity in the mid-1980's as demand continues to grow. One producer reportedly forecasted an increase in capacity to 500 x $10^6$ lb/yr by the mid-1980's (Journal of Commerce, 18 Sept. 1979, p. 1), but a major producer contacted by Winzler and Kelly felt that this figure was perhaps appropriate for all completion fluids, not just calcium bromide completion fluids. Inflating the estimated current (late 1980) level of calcium bromide production of 130 x $10^6$ lb/yr by 15%/yr for five years indicates a 1985 production level of roughly 261 x $10^6$ lb/yr (110 x $10^6$ lb contained bromine). A recent report indicates that calcium bromide demand is growing even faster: 20%/yr (Chem. Mark. Rep., 6 July 1981, p. 25).

### 2.5.3 Environmental Hazards

Because calcium bromide ($CaBr_2$) is a non-volatile inorganic salt, emissions to the atmosphere during production and use are unlikely. During its production, low-level emissions of bromine are to be expected.

Calcium bromide does not pose significant human-health or ecological concerns at low concentrations, nor do the low-level bromine emissions produced during calcium bromide production. Calcium bromide is not likely to occur in the environment in high concentrations, except through accidental spills and perhaps the discharge of drilling fluids at sea, which result in only temporarily high concentrations over limited areas. Drilling fluids disposed of on land would likely be ponded with the cuttings in a relatively impermeable pit (clay-lined, for example). However, some drilling muds are applied to agricultural land as a means of disposal. If calcium bromide were mixed with drilling mud and applied to land, contamination of ground and surface waters might occur and bromine might accumulate in plants.

In light of the uncertainty over disposal practices for calcium bromide drilling fluid and the potential resulting environmental effects, further study into this matter would be appropriate.

## 2.6 Bromine Chloride

### 2.6.1 Introduction

In the search for water and wastewater disinfectants that do not present problems of fish toxicity, trihalomethane formation, and poor virucidal activity, as does chlorine, bromine chloride has emerged as a prime candidate. Recent research indicates that, compared to chlorine, bromine chloride is a more effective virucide and an equally effective bactericide, and it results in a lower oxidant residual (Keswick et al., 1980). Dow Chemical Co. produces bromine chloride for use in wastewater and cooling water, but, according to a spokesman, Dow does not presently recommend bromine chloride for drinking water because of its low residual compared to chlorine. (Residual disinfectant in drinking water is desirable to protect the supply against contamination downstream of the point of disinfection.)

Bromine chloride is described by Dow as a heavy, fuming dark-red liquid with a sharp, penetrating odor (Dow, 1978). Some of its properties are presented in Table 2.6-1. Bromine chloride is classified as a powerful oxidizer, as reacting vigorously with combustible materials (Hawley, 1977), and as being a corrosive liquid (Dow, 1978). In both the gaseous and liquid states, it exists in equilibrium with free bromine and chlorine (Dow, 1978).

Bromine chloride hydrolyzes exclusively to hypobromous acid (HOBr) and HCl, and in wastewater, BrCl and HOBr react with ammonia to form bromamines and hydrogen chloride (Dow, 1978).

### 2.6.2 Production and Consumption

According to industry representatives, Dow Chemical Company is currently the only domestic producer of bromine chloride, utilizing its new 30 x $10^6$ lb-per-year capacity facility at Magnolia, Arkansas (see also Chem. Mark. Rep., 22 Oct. 1979, p. 7). Dow's current level of production has not been disclosed, but if its plant were operating at 80 percent of capacity, production would be 21 x $10^6$ lb/yr (17 x $10^6$ lb Br/yr). Although Dow's facility at Magnolia, Arkansas was designed specifically for bromine chloride production, other facilities have the potential for bromine chloride production with relatively minor modifications.

Dow's market for bromine chloride is created largely by regulations requiring reduced chlorine residual in aqueous effluents to protect fish. Dow reportedly designed its bromine chloride facility to meet only existing demand (Chem. Mark. Rep., 22 Oct. 1979, p. 7). If EPA's proposed regulation to limit total residual chlorine discharged in once-through cooling water and in cooling-tower blowdown from steam electric power plants to 0.14 mg/l (45 Fed. Reg. 68328, 14 Oct. 1980) is promulgated, demand for bromine chloride will likely increase, although forecasts are not available.

In 1974, 2.75% of the chlorine produced domestically was used for wastewater chlorination (presumed to include sewage and cooling water) (Mitchell, 1981). Current production is roughly 2.2 x $10^{10}$ lb (Chem. & Engr. News, 2 Mar. 1981, p. 11) implying a demand for wastewater chlorination of 605 x $10^6$ lb. The bromine chloride molar equivalent of this amount of chlorine is 980 x $10^6$ lb, indicating a very high potential demand for bromine chloride. However, because the cost effectiveness of bromine chloride depends, among other things, on ammonia levels in the wastewater (Mills, 1980)--ammonia rapidly consumes bromine chloride's oxidant residual causing a higher dosage requirement--much of this potential will not be realized. Also, bromochlorination has a substantially greater energy requirement than does chlorination

Table 2.6-1. Chemical and Physical Properties of Bromine Chloride

| | |
|---|---|
| Chemical Formula | BrCl |
| Synonyms | Chlorine bromide |
| Molecular Weight | 115.3 |
| Boiling Point, °C | 5 |
| Melting Point, °C | -66 |
| Vapor Pressure @ 20°C | 30 psig (= 44.7 psia = 2316 mm Hg) |
| Specific Gravity @ 20°C | 2.34 |
| Solubility | 85 g/100 g water; sol. in carbon disulfide and ether[a] |
| Stability | Decomposes with evolution of chlorine at 10°C[a] |

---

Source: Dow, 1978, except as noted otherwise.

[a] Source: Hawley, 1977.

or chlorination-dechlorination (Mills, 1978). The data in Table 2.6-2 illustrate bromine chloride's cost disadvantage in sewage treatment compared to chlorination, chlorination-dechlorination, with sulfur dioxide and chlorination-dechlorination with $SO_2$-post aeration.

### 2.6.3 Emissions

We know of no emissions data for bromine chloride. Once released, it would likely at least partially decompose to bromine and chlorine. Low-level emissions of bromine chloride are not a significant concern because it is not likely to be hazardous at low concentrations, although it might contribute to the accumulation of bromide in pine trees growing near the bromine-producing facilities in southern Arkansas (Tainter and Bailey, 1980).

All of the bromine chloride produced, except for the small amounts lost during production, use, and accidental spills, is intentionally introduced to bodies of water.

### 2.6.4 Environmental Fate

In water, BrCl hydrolyzes to hypobromous acid (HOBr) and HCl, and in the presence of ammonia, bromamines (primarily mono- and dibromamine: $NH_2Br$ and $NHBr_2$, respectively) are formed, which are more potent bactericides and virucides than are chloramines (see for example, Keswick et al., 1980).

An industry spokesman stated that bromamines are destroyed much more quickly by reductants in water than are chloramines, resulting in much lower levels of bromamines than chloramines in receiving waters. This statement is confirmed in the scientific literature (e.g., Keswick et al., 1980).

Brominated organics are formed during chlorination and bromochlorination. An extensive review of the subject concluded (NAS, 1979c), "tenuous evidence suggests that the total THM [trihalomethane] yield would be greater for bromine than for chlorine." Groninger and Mills (1980) reported that the yield of bromoform from bromination of sewage effluent was much greater than the yield of chloroform from chlorination but that the bromoform levels were reduced by roughly 50 to 90% 100 yd downstream of the outfall (accounting for dilution). The loss of bromoform was attributed to evaporation and to chemical decomposition, which is said to be more rapid for bromoorganics than chloroorganics because of the weaker carbon-bromine bond (see also NAS, 1979c). This work is in support of the Dow statement (Dow, 1978), "the trace amounts of brominated organics produced during disinfection are generally less stable than their chlorine analogs and should not persist long enough to cause problems in receiving waters."

Table 2.6-2. Total Treatment Cost for Sewage Disinfection Alternatives [Cost Expressed as Cents/1,000 gal Treated (Capital Costs Included)]

| | | Plant Size (mgd) | | |
|---|---|---|---|---|
| | Disinfection Alternatives | 1 | 10 | 100 |
| 1. | Chlorination | 3.6 | 1.5 | 0.77 |
| 2. | Chlorination-Dechlorination with $SO_2$ | 4.5 | 1.9 | 0.96 |
| 3. | Chlorination-Dechlorination with $SO_2$-Post Aeration | 7.8 | 2.5 | 1.3 |
| 4. | Chlorination-Dechlorination with Activated Carbon | 19.1 | 8.7 | 3.4 |
| 5. | Chlorobromination (BrCl) | 4.4 | 2.4 | 1.6 |
| 6. | Ozonation (from oxygen) | 8.0 (air) | 4.2 | 3.1 |

Source: Mills, 1978.

Minear and Bird (1980) reported that the addition of bromide ion caused an increased yield of trihalomethanes during chlorination. This result was not found by Groninger and Mills (1980), who reported that chlorobromination of water containing humic acids produced a level of bromoform similar to that produced by the chlorination of the same water containing added bromide (30 ppm), and that chloroform production was low in both cases. On the other hand, Sweetman and Simmons (1980) found that 2,4,6-tribromophenol was formed to a greater extent by the action of hypochlorous acid (HOCl) and bromide ion on phenol than by the action of hypobromous acid (HOBr), the hydrolysis product of bromine chloride.

We conclude that additional research is needed to reconcile conflicting evidence and to verify the claims that bromochlorination creates no greater hazard from halogenated organic compound formation than does chlorination.

### 2.6.5 Health Effects

According to industry sources, BrCl is just as toxic to humans as $Cl_2$, which has an 8-hr time-weighted average occupational limit of 1 ppm, as does $Br_2$ (NIOSH/OSHA, 1978). However, BrCl is supplied under low pressure as a corrosive liquid, not as a compressed gas as is chlorine. Therefore, if a container of BrCl (supplied in 1-ton tanks or in tank cars) were punctured, the gas would vaporize and disperse more slowly than would chlorine, allowing more time for emergency activities to be implemented. In this respect, BrCl is safer than $Cl_2$.

At present, little or no BrCl and little $Br_2$ is used for disinfecting drinking water, so the issue of inadvertent trihalomethane production is not a major one. Miller (1980) noted that tribromomethanes seem to be more mutagenic than trichloromethanes.

### 2.6.6 Ecological Effects

Residual bromine chloride is toxic to aquatic organisms, as is chlorine (see for example Ward and DeGrave, 1978a). Ward and DeGrave (1978b) showed that residual BrCl at least up to a concentration of 0.017 mg/l had no lethal effects on fathead minnows during their life cycle. Liden et al. (1980) found that residual BrCl at least up to 0.08 mg/l had no lethal effect on four species of estuarine organisms (two fish and two bivalves) during 15- to 20-day tests. In acute toxicity tests, chlorinated wastewater was more toxic than the same wastewater treated with bromine chloride, except for salmonid fishes, which were more susceptible to bromine chloride (Ward and DeGrave, 1980).

An industry source stated that bromamines and chloramines were equally toxic to fish but that bromamines degrade much more rapidly than chloramines. See Section 2.6.4.

Burton and Margrey (1978) concluded that chlorine residual was likely more toxic to grass shrimp than was bromine chloride, but that more study was needed to establish bromine chloride as being more environmentally acceptable than chlorine.

The toxicity studies reported in the literature do not take into account the rapid decomposition of residual bromine chloride in wastewater: 80 to 90% within 5 min compared to 30% for chlorine residual (Keswick et al., 1980). Whether or not similar behavior occurs in natural surface waters is an area for investigation, perhaps by in situ bioassay.

### 2.6.7 Implications for EPA

The adverse effects of disinfecting sewage effluents, cooling water, and drinking water is already under study by EPA. Additional research into the extent of brominated organics formation during bromochlorination compared to chlorination and into the stability of brominated organics compared to chlorinated organics would be useful. Also, although bromochlorination appears to be less harmful to aquatic biota than chlorination, the point has not been fully demonstrated. Most studies have compared the toxicity of BrCl to $Cl_2$, not taking into account the far greater rate of disappearance of the former (including bromamines) from water containing oxidizable substances.

## 2.7 Vinyl Bromide

### 2.7.1 Introduction

Ethyl Corp. (1979) recently characterized vinyl bromide as follows:

> VBr is now commercially quite important. It can be co-polymerized with other monomer chemicals, thus incorporating stable bromine atoms along the polymer chains of plastic and fibers. Federal laws require fire-resistant qualities in many garments and also in construction materials. Since bromine-bearing plastics and fibers show excellent fire-retardant qualities, they have become important materials for meeting specifications of fire regulations. This predominant and growing use first attained full commercial development in 1968.

And LeBlanc (1977) provided the following characterization:

> Vinyl bromide is a reactive flame retardant used in small amounts as a comonomer with acrylonitrile and other vinyl monomers in modacrylic fibres. Modacrylic fibres containing vinyl bromide are used in fabrics and fabric blends with polyesters for children's sleepwear and other clothing, home furnishings and industrial applications.

A modacrylic fiber produced by Monsanto that is used primarily in children's sleepwear contains 79 to 81% acrylonitrite, 9% vinyl bromide, 8% vinylidene chloride, and 2 to 4% other (SRI, 1976). Badische Corp. uses vinyl bromide (VB) to produce acrylic and modacrylic carpet fiber only (Charter, 1979).

VB is a colorless gas and liquid, with a boiling point of 16°C and a pungent odor. It is available from Ethyl Corp. as a liquid under slight pressure. VB is said to have relatively low reactivity because the double bond acts as a resonance hybrid between carbons and between carbon and bromine atoms, making the bromine atom more stable than if the C-Br bond were purely single (U.S. EPA, 1980a, p. 279). The properties of VB are summarized in Table 2.7-1.

### 2.7.2 Production and Consumption

Ethyl Corp. was the only domestic manufacturer of VB as of early 1979, its production plant being near Magnolia, Arkansas (Ethyl Corp., 1979, pp. 1 and 9). It was stated in 1976 (Ethyl Corp., 1976, p. 2) and restated in 1979 (Ethyl Corp., 1979, p. 1) that production was over 5 x $10^6$ lb/yr and that uses other than in polymeric fibers, such as in the manufacture of pharmaceuticals, pesticides, and other chemicals, were expected to grow. Assuming that production in 1976 was roughly 5 x $10^6$ lb and that growth has occurred since then at a healthy rate of 10%/yr, current production would be roughly 8 x $10^6$ lb/yr.

One industrial user of VB stated that, to the best of its knowledge, Ethyl Corp. was the sole domestic producer and Monsanto Co. and Badische Corp. the only industrial users of VB. Badische Corp. uses VB only to produce acrylic and modacrylic carpet fiber at Williamsburg, VA (Charter, 1979). Badische reportedly consumed between $10^5$ and 1.5 x $10^6$ lb/yr as of 1976 and has been using VB since 1970 (U.S. EPA, 1980a, p. 281).

Mara and Lee (1978, p. 13) stated that VB was produced by Ethyl Corp. at Magnolia and by Dow Chemical Co. in Midland, Michigan, but this does not agree with reports that Ethyl is the sole producer (Ethyl Corp., 1979; Badische Corp., 1979; U.S. ITC, 1979).

### 2.7.3 Emissions

VB is produced by the pyrolysis of ethylene dibromide (EDB), which is fed continuously, in the presence of caustic. Hydrogen bromide is released, which, along with unreacted EDB, is collected and recycled. Ethyl's production facility is located outdoors. The VB product is shipped out in tank cars (Bales, 1977; Ethyl Corp., 1979).

Table 2.7-1. Chemical and Physical Properties of Vinyl Bromide

| | | |
|---|---|---|
| Chemical Formula | $CH_2 = CHBr$ ($C_2H_3Br$) | |
| Synonyms | Bromoethylene; Bromoethene | |
| CAS Registry Number | 593-60-2 | |
| NIOSH RTECS Number | KU 84000 | |
| Molecular Weight | 106.96 | |
| Boiling Point, °C at 760 mm Hg | 15.8 | |
| Melting Point, °C | -139.5 | |
| Vapor Pressure | psia | mm Hg |
| 0°C | 8.2 | 424.2 |
| 20°C | 17.0 | 879.4 |
| 40°C | 31.6 | 1634.7 |
| Density of liquid, g/ml at 20°C | 1.522 | |
| Density of vapor (air=1), temp. not specified | 3.7 | |
| Solubility | Insol. in water; sol. in alcohol, ether, acetone, benzene, and chloroform | |
| Stability | Polymerizes rapidly in light | |
| Flammability | Inflammable[a] | |
| Flash Point (COC) | None[a] | |
| Fire Point (COC) | None[a] | |
| Appearance | Colorless liquid and gas | |
| Odor | Pungent | |
| Heat of vaporization, cal/g | 54.9 | |
| Heat of fusion, cal/g | 12.3 | |
| Corrosivity | Non-corrosive when dry at ambient temp. | |
| Conversions | | |
| lbs/gal at 20°C | 12.7 | |
| kg/l at 20°C | 1.522 | |
| 1 ppm in air | 4.4 $mg/m^3$ | |
| Vinyl Bromide content of Ethyl Corp.'s Product | 94.6%, exclusive of stabilizer | |

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[a] Ethyl Corp. found that vinyl bromide is moderately flammable at vapor concentrations of 6 to 15%, even though standard flash- and fire-point tests indicate that it is non-flammable.

Source: IARC, 1979; CRC, 1976; Ethyl Corp., 1974.

An industrial hygiene survey of Ethyl Corp.'s VB facility revealed that employee exposure to VB is maintained at low levels by several measures: containment of processes and process materials; minimizing leaks; ventilation; separation of the plant from the control room; use of vapor-return lines when filling tank cars; and good work practices (Bales, 1977). The measures that reduce VB releases to the workplace will also reduce its release to the general environment. Other specific control measures have been enumerated, including: chilled EDB absorber that prevents VB emissions to the atmosphere; quality-control sampling from a continuous loop eliminates the need to waste significant amounts of VB; closed-system addition of inhibitor; purge of loading hose to prevent VB release when disconnecting; and, as is common in the chemical industry, all pumps have mechanical seals (Ethyl Corp., 1979).

During a sampling program, a trace of VB was detected in the air at Ethyl's plant[1], and none was detected in the soil (Pellizzari et al., 1978a).

Using the methodology in Appendix B and assuming $8 \times 10^6$ lb/yr production, 15 days downtime, and an emission rate of 1% of production, we calculated a 10-min ground-level concentration 500 m downwind from the plant of 0.12 $mg/m^3$ (27 ppb). Considering that only a trace of VB was detected on the site during an ambient sampling study and that the plant employs effective control measures, the actual emission rate may be substantially lower than 1% of production.

VB concentrations in the routine work areas of the Dow Badische Company's Williamsburg plant average under 1 ppm. Considering that practices that reduce workplace concentrations are likely to also reduce emissions to the ambient air (Margler et al., 1979, p. 1157) and that all of the vinyl bromide consumed at the Badische plant is co-polymerized, emissions from this plant are likely quite low. We have no information on the operations of Monsanto Co. Dow Badische, Ethyl Corp., and Monsanto have in-house exposure guidelines of 1 ppm (8-hr time-weighted average) (Charter, 1979; Ethyl Corp., 1979; Chem. & Engr. News, 14 Nov. 1977, p. 20).

A recent study reported that VB was not released in detectable amounts from acrylic or modacrylic fibers under normal conditions (Finkel et al., 1979).

We have found no measurements of vinyl bromide in water, and we know of no major aqueous waste streams. VB's high volatility would help to mitigate discharges to water.

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[1] Pellizzari et al. (1978a) actually stated that a trace of methyl bromide was detected, but we believe that vinyl bromide was intended.

### 2.7.4 Environmental Fate

We have found no information on the stability of VB in air, water, or soil, or on its biomagnification potential. This lack of information was also observed by EPA (U.S. EPA, 1980a, p. 287). However, that liquid VB is attacked by oxygen (Ethyl Corp., 1974) and that it polymerizes rapidly in light (Pollock and Stevens, 1965) suggests at least a modest degree of instability in the environment.

The chemical behavior of vinyl chloride (VC) -- the chlorinated analog of vinyl bromide, which is much more important commercially than vinyl bromide and whose potential hazards have been known longer than vinyl bromide's -- in ambient air has not been thoroughly characterized. VC has been shown in laboratory photochemical chamber experiments to react with high concentrations of $NO_2$, $O_3$, NO and hydroxyl radicals, yielding carbon monoxide, formaldehyde, formic acid, formyl chloride and hydrogen chloride (Gay et al., 1976). When potential reactants are at low concentrations or are absent, VC can be quite stable, with little potential for autodegradation in sunlight. An atmospheric half-life for VC of roughly 4 hr was suggested by a panel of experts (Margler et al., 1979). In the absence of information on VB, the data on VC may serve as a guide.

### 2.7.5 Health Effects

VB is a moderatley toxic substance. Its oral median lethal dose in rats is 500 mg/kg, and the recommended Threshold Limit Value in air is 250 ppm, based on non-carcinogenic or non-teratogenic effects. Based on VB's carcinoginogenic potential, NIOSH has recommended an 8-hr time-weighted average of 1 ppm and a 15-minute ceiling of 5 ppm (NIOSH, 1978).

VB is mutagenic in *Salmonella* (a bacterium) and *Tradescantia* (a plant) (NIOSH/OSHA, 1978a) and carcinogenic in rats (Ethyl Corp., 1979). The Occupational Safety and Health Administration feels that the carcinogenicity of VB in test animals has been firmly established, with a significant increase (10 to 15%) in liver angiosarcomas in rats observed even at 10 ppm (Kang, 1980).

The toxicology of VB has been reviewed by U.S. EPA (1980a, p. 282), IARC (1979), and Ethyl Corp. (1979).

### 2.7.6 Ecological Effects

We have found no information on the environmental toxicity of VB or on its biomagnification potential. Considering that releases to the environment appear to be quite low, the ecological effects may be insignificant. However, the potential for localized damage exists if VB is being discharged to surface waters. In this regard, Pellizzari et al. (1978a) found no VB in soil, sediment, water, milk, or vegetation samples taken near the production facility.

### 2.7.7 Pollution Control Technology

The controls discussed in the Emissions section are effective at reducing the emissions to the ambient air. Emissions could be further reduced by implementing still more rigorous containment practices or by enclosing the plant and venting through a scrubber of some type, a chiller or adsorber, for example.

### 2.7.8 Analytical Methods

Pellizzari et al. (1978b) measured vinyl bromide in ambient air by trapping the VB in a short carbon column and transferring the VB, through a series of intermediate steps, into a high-resolution glass gas-chromatographic column combined with a mass spectrometer (GC/MS). The limit of detection for VB at an ambient temperature of 15.5°C was 6.5 ng/m$^3$ (1.5 ppt). Volatile brominated compounds were measured in soil, sediment, water, milk, and vegetation by diluting the samples in water and purging them (after shredding in a blender in the case of vegetation) with an inert gas. The vapors were then trapped on Tenax GC for analysis by GC/MS.

### 2.7.9 Risk Assessment

Mara and Lee (1978) made crude estimates of population exposure to ethylene dibromide (EDB) at Magnolia, Arkansas based on an estimated ambient concentration of 3 ppb 100 m from the Dow Chemical Co. plant there. Such an ambient level is roughly similar to vinyl bromide concentrations that might be expected on an annual average downwind from Ethyl Corp.'s production plant near Magnolia. We translated the data of Mara and Lee (1978) into a total exposure to EDB of 375,000 person-ppt, which resulted from an assumed production at Magnolia of 4.4 x 10$^8$ moles of EDB per year (82 x 10$^6$ kg = 180.4 x 10$^6$ lb), or 8.5 x $^{-4}$ person-ppt per mole. The exposure rate in ppt should be proportional to the emission rate in moles. We applied the estimated production rate for VB of 3.4 x 10$^7$ mole/yr (8 x 10$^6$ lb) to the rate of 8.5 x 10$^{-4}$ person-ppt per mole for EDB to get an exposure of 28,900 person-ppt.

Assuming that VB has the same carcinogenic risk factor as EDB, and calculating cancer incidence as for EDB (Appendix D), we derived an estimated cancer incidence surrounding Ethyl's Magnolia plant of 6.7 x 10$^{-4}$ cancer/yr. Thus, if the assumptions hold, a rather low risk exists. Because of the uncertainties involved, the major ones being the carcinogenic potency of VB in humans and exposures, this estimate could be off by orders of magnitude.

Except for accidental releases, little or no threat to human health is apparent from non-occupational exposures to VB. Even for persons residing very close to one of the facilities that produce or use VB, exposures do not appear to be significant, although no hard data exist on which to base this assertion.

Considering that VB caused a 10 to 15% increase in liver angiosarcomas in rats at 10 ppm, a 1-ppm occupational level might not afford sufficient protection.

### 2.7.10 Implications for EPA

Our assessment indicates that the risk to the public and to the environment from the production and utilization of VB is low. However, major aspects of the assessment are based on scanty data, which could be improved by an on-site emission inventory of the plants producing and using VB, by the Carcinogen Assessment Group performing a carcinogenic risk assessment (i.e., low-dose extrapolation to humans) for VB, and by performing a detailed population risk assessment. More information may come from a study that the Arkansas Dept. of Health is planning of the bromine industry in southern Arkansas (Wise, 1981).

If a reduction in VB emissions were desirable, a likely avenue for regulation would be Seciton 112 of the Clean Air Act (National Emission Standards for Hazardous Air Pollutants), as for vinyl chloride.

## 2.8 Dibromochloropropane (DBCP)

### 2.8.1 Introduction

DBCP was used as a liquid soil fumigant against nematodes on various crops (NIOSH, 1978b). All EPA pesticide registration for DBCP, except Hawaiian pineapples, were suspended on 29 October 1979. The situation was such in Hawaii that EPA's Administrator felt that the risks of using DBCP on pineapples there were small and did not outweigh the benefits (BNA, 1979a, p. 1507).

DBCP is a yellow-orange to brown colored liquid with a pungent odor and moderately high boiling point. Salient characteristics are presented in Table 2.8-1.

### 2.8.2 Production and Consumption

Recent production and consumption data are unavailable, although the U.S. ITC reported 8.6 x $10^6$ lb production in 1969 and 15.2 x $10^6$ lb sales in 1972 (Fowler, 1980). Dow was reported as the only domestic producer in 1978 (U.S. ITC, 1979), and no firms reported production for 1979 (U.S. ITC, 1980). Amvac Chemical Corp. was the last known manufacturer, producing DBCP in Los Angeles for export. It was reported in 1979 that Amvac was producing 2,500 gal/d of DBCP (Taylor, 1979a). At a density of 2.1 g/$cm^3$, 16 x $10^6$ lb/yr would be produced at this rate (if pure) under continuous operation, actual capacity likely being substantially less because of down-time. SRI (1980) estimated Amvac's annual production capacity at 25 x $10^6$ lb/yr.

Table 2.8-1. Chemical and Physical Properties of DBCP

| | |
|---|---|
| Chemical Formula | $BrCH_2CHBrCH_2Cl$ ($C_3H_5Br_2Cl$) |
| Synonyms | 1,2-dibromo-3-chloropropane; dibromochloropropane |
| CAS Registry Number | 96-12-8 |
| NIOSH RTECS Number | TX8750000 |
| Molecular Weight | 236.36 |
| Boiling Point | 199°C |
| Vapor Pressure | Under 1 mm Hg at 21°C |
| Specific Gravity | 2.09 with respect to water at 14°C |
| Solubility | Miscible with aliphatic and aromatic hydrocarbons, isopropyl alcohol, 1,2-dichloropropane, tetrachloroethylene, 1,1,2-trichloroethane, and oils |
| Flash Point | None |
| Fire Point | None |

Source: NIOSH, 1978b

Amvac is required to collect and submit air samples to the South Coast Air Quality Management District for DBCP assay whenever it produces DBCP. Because no samples have been submitted since March 1980, it may be assumed that production has not occurred since then (Holland, 1980). When contacted, Amvac would not discuss production in significant detail.

The future of DBCP use in the U.S. depends on the longevity of the suspension. If not voided by challenges, the domestic use of DBCP will remain low or nil. However, its production may continue unaffected by the suspension if foreign markets exist. Also, suspicion exists that DBCP is being sold and used illegally in California (Chem. Week, 6 Feb. 1980, p. 21).

### 2.8.3 Emissions

Pellizzari et al. (1978a) measured up to 6,653 ng/m$^3$ (0.68 ppb at 20°C) DBCP in the ambient air at the Dow Chemical Plant near Magnolia, Arkansas. The California Air Resources Board and the South Coast Air Quality Management District monitored the air adjacent to the Amvac Chemical Co. plant in the Los Angeles area (City of Commerce). The monitoring station was approximately 300 feet from the reactor building (Bonamassa, 1979). The result of nearly 50 monitoring periods (4 to 24 hr long) from 11 May 1979 to 15 June 1979 was that the average DBCP concentration measured was 0.09 ppb (40 samples), with 9 other samples below the detection limit of 0.01 ppb. The highest level was 0.69 ppb, and the next highest was 0.17 ppb (Camarena, 1979). At the time of these measurements, emissions may have been as high as 1 ppm in the exhaust from the reactor (Nichols, 1980). Subsequently, Amvac agreed with Cal/OSHA to maintain its air purification system in proper condition, which would limit the concentration of DBCP in the reactor exhaust to 10 ppb (Misc., 1979). The Air Resources Board (Nichols, 1980) and the SCAQMD (Metzley, 1981) feel that air emissions from the facility are well controlled.

Emissions would also occur during the application of DBCP, but because of its relatively low vapor pressure, atmospheric emissions and off-site exposures would likely be low.

### 2.8.4 Environmental Fate

Two years after its use in California was banned, DBCP was found in well-water in the Central Valley (Chem. & Engr. News, 25 June 1979, p. 24; Taylor, 1979b; BNA, 1979b). An average of 4.6 ppb, with a maximum concentration of 39 ppb, was reported in well water (Chem. & Engr. News, 25 June 1979, p. 24), and one of seven municipal wells in the city of Dinuba, Tulare County was reportedly closed after 9 ppb was discovered in its water (Los Angeles Times, 29 May 1979, Part 1, p. 2). Groundwater contamination with DBCP is therefore a potential threat to human health.

We have found no data on DBCP's stability in water, soil, or air. However, the discovery of DBCP in well-water in areas of its use and in air around its production facilities demonstrates that it is sufficiently stable so as not to preclude environmental hazards.

DBCP residues have been detected in foods grown in soils fumigated with DBCP formulations. Up to 0.20 ppm DBCP was measured in radishes and up to 1.55 ppm in carrot roots (NIOSH, 1978a). Except in root crops, contamination may be only on the plant surface, resulting from contact with contaminated soil or condensation from air onto plant surface (Kempter and Bernstein, 1978).

### 2.8.5 Health Effects

An 8-hr time-weighted average concentration of 1 ppb (an unusually low standard) was established as the occupational exposure limit for DBCP in early 1977 based on its ability to cause sterility in males occupationally exposed and on its carcinogenic activity in rats and mice (Chem. Week, 3/22/77, p. 25). DBCP tested positive in NCI's carcinogenetic bioassay (NCI, 1977), and the IARC concluded that DBCP was a carcinogen in test animals (NIOSH, 1978). Concern also exists over potential damage to the kidneys and liver. Median lethal doses reported for test animals range from 60 to 440 mg/kg. The toxicology of DBCP has been reviewed by NIOSH (1978b).

### 2.8.6 Ecological Effects

We have found no information on the ecological effects of DBCP production and utilization. Ecological effects could occur through direct action on soil organisms and indirectly through food-chain magnification. DBCP might contribute to ozone depletion in the stratosphere, but its low consumption rate (even before awareness of its health hazards developed) compared to other chlorinated and brominated compounds suggests its relatively low importance in this regard.

### 2.8.7 Pollution Control Technology

Emissions are controlled to a high degree at Amvac Chemical Corp.'s plant near Los Angeles, California. Critical areas where substantial leakage into the workplace could occur are under vacuum so that nearly all fugitive DBCP vapors are vented to the scrubber, which consists of a multistage carbon adsorber, before the air is vented to the outside air. Allyl chloride, a reactant, is controlled in a separate scrubber placed before the DBCP scrubber. An electron capture detector placed ahead of the last carbon stage indicates when the adsorber requires attention (Metzley, 1981). The air purification system limits DBCP emissions to 10 ppb (Misc., 1979).

### 2.8.8 Analytical Methods

The South Coast Air Quality Management District (Los Angeles County, California) assays air for DBCP down to 0.01 ppb by adsorbing the DBCP in the air in charcoal tubes, desorbing into liquid phase with 1% carbon disulfide in benzene, and injecting the liquid phase into a gas chromatograph with electron capture detector (Moore, 1981). A similar procedure was reported to NIOSH by Shell Development Company, except that Florisil and hexane replaced charcoal and carbon disulfide-benzene, respectively. The "useful range" was reported as 1 ppb to 100 ppb (NIOSH, 1978b).

### 2.8.9 Risk Assessment

The populations at risk from DBCP are those persons occupationally exposed during its production, storage, transportation, and usage, and those non-occupational groups exposed through the air near production and usage areas, through food grown in contaminated soil, and through contaminated drinking water.

Occupational exposures are controlled by the 1 ppb standard, except during storage, distribution, and application of DBCP.

Non-occupational exposure near Amvac's production facility is well-controlled by the emission limit of 10 ppb established by Cal/OSHA. The average measurable concentration adjacent to the plant over a one-month period was 0.09 ppb. Such a level of exposure would result in a very small risk of contracting cancer, if DBCP is indeed carcinogenic in humans. For example, in the risk assessment for vinyl bromide, if a ground-level concentration of 0.09 ppb 100 m from the plant were used instead of 3 ppb, the calculated cancer incidence would be $2 \times 10^{-5}$/yr rather than $6.7 \times 10^{-4}$/yr; that is, in a million years, 20 cancers might result.

As part of its Rebuttable Presumption Against Registration (RPAR) process, EPA very roughly estimated the cancer incidence that might be attributable to ingestion of contamined food to inhalation and dermal contact by applicators, and to inhalation during re-entry and spill cleanup (Kempter and Bernstein, 1978). An estimated 2008 cancers per year might result from ingestion of contaminated crops: 68% from carrots, 57% from peanuts, 5% from melons, 5% from tomatoes, and 17% from all other (ibid., p. 170). Application operations might cause one cancer case per year (ibid., p. 173), and re-entry, spill cleanup, and dermal exposure many fewer (ibid., p. 174). This assessment does not account for the potential hazards of drinking contaminated well-water.

### 2.8.10 Implications for EPA

EPA has suspended all uses of DBCP except on pineapple fields in Hawaii (BNA, 1979a). The use on pineapples could continue, and suspended uses could be allowed again if industry demonstrates to EPA that the hazards, including farmworker exposure and exposures from food and water, are acceptable (Kempter, 1980). Emissions from Amvac Chemical Corp.'s plant are tightly controlled because of conditions imposed by Cal/OSHA. Further EPA involvement beyond the current level appears unnecessary.

## 2.9 Brominated Anilines and Nitro Anilines

### 2.9.1 Introduction

In May 1980, JRB Associates, Inc. submitted a report to EPA's Office of Toxic Substances providing a "level I" materials balance for 44 aniline-based compounds (Hall et al. 1980). The study included five brominated anilines and nitroanilines -- 4-(or p-) bromoaniline (BA); 2,4,6-tribromoaniline (TBA); 2,6-dibromo-4-nitroaniline (DBNA); 2-bromo-4,6-dinitroaniline (BDNA); and 2-bromo-6-chloro-4-nitroaniline (BCNA) -- plus aniline hydrobromide (AHB). Very little information on these compounds was found. Of the 44 compounds specified in the task order, no information was found on three, all of which were brominated -- 2,4,6-tribromoaniline hydrobromide; 2-bromo-4,6-dichloroaniline; and 4-bromo-3, 5-dichloroaniline -- none of which are listed in the 1980-81 OPD Chemical Buyer's Guide (OPD, 1980). This section presents the findings of Hall et al. (1980) for brominated anilines, supplemented with other information where noted.

The only information on uses of brominated anilines in Hall, et al. (1980) was the statement that they seem to be used primarily by the dye industry. Because some of them are listed by the U.S. ITC (1979) as "cyclic intermediates," we assume that they are indeed used largely as intermediates in aniline-based dye production. BA is said to be used in the preparation of azo dyes and dihydroquinazolines (Merck, 1976, p. 180).

Little information is readily available on the chemical and physical properties of bromoanilines. Table 2.9-1 summarizes the available data for the bromoanilines discussed in this section.

### 2.9.2 Production and Consumption

For BA and TBA, Hall et al. (1980) provided producers' names for the years 1974 through 1978. They reported that only Aldrich Chemical (Milwaukee, Wisconsin) produced BA in 1978 and only Eastman Kodak (Rochester, New York) during 1974 through 1977; however, the U.S. ITC (1979 and 1980) reported Eastman Kodak as the sole producer in 1978 and 1979. Parish Chemical Company (Orem, Utah) has advertised recently that it makes BA "by the ton" (see for example Chem. Engr. News, 17 Nov. 1980, p. 50). TBA was reportedly produced by Kodak Park Division (Rochester, New York) and by Great Lakes Chemical (West Lafayette, Indiana) during 1977, and no data were available for other years (Hall et al. 1980). TBA was not listed as being produced in reportable quantities in 1979 (U.S. ITC, 1980), but it is available from American Hoechst, Great Lakes, and E.B. Knight (OPD, 1980). Firms producing DBNA, BDNA, and BCNA during 1978 are identified in Table 2.9-2.

Table 2.9-1. Chemical and Physical Properties of Some Brominated Anilines

| | Chemical Formula | Molecular Weight | Melting Point (°C) | Boiling Point (°C) | Solubility |
|---|---|---|---|---|---|
| BA | $C_6H_6BrN$ | 172.03 | 66.4 | Decomposes | Insol. in water<br>Sol. in alcolol-ether |
| TBA | $C_6H_4Br_3N$ | 329.83 | 122 | 300 | Insol. in water. Slightly sol. in alcohol and sol. in ether and chloroform. |
| DBNA | $C_6H_4Br_2N_2O_2$ | 295.93 | 207 | No data | Slightly sol. in water; sol. in acetic acid. |
| BDNA | $C_6H_4BrN_3O_4$ | 262.03 | 153-154 | Sublimes | Very sol. in hot alcohol and hot acetone; sol. in hot acetic acid; slightly sol. in water[a] |
| BCNA | - - - - - - - - - No data - - - - - - - - - - - - - - - - - | | | | |
| AHB[b] | $C_6H_7N\cdot HBr$ | No data | 286 | No data | Sol. in water and alcohol |

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Source: CRC, 1976, except where noted otherwise.

[a] Source: Hall et al., 1980.

[b] Source: Merck, 1976.

Table 2.9-2. Producers of DBNA, BDNA, and BCNA During 1978

| Producers | DBNA | BDNA | BCNA |
|---|---|---|---|
| American Hoechst, Coventry, RI | X | X | X |
| Martin-Marietta, Sodyeco, NC | X | X | |
| Salsbury Labs, Charles City, IA | X[a,c] | | |
| Toms River Chemical Co., Toms River, NJ | | X[a,c] | |
| American Color & Chemical Corp., Reading, PA | | X[b,c] | |
| GAF Corp., Chattanooga, TN | | X[b,c] | |

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Source: Hall et al., 1980 and U.S. ITC, 1979, except as noted otherwise.

[a] Not listed by U.S. ITC, 1979.

[b] Not listed by Hall et al., 1980.

[c] Not listed by U.S. ITC (1980) as a producer in 1979.

Hall et al. (1980) reported that no quantitative production and use data were available for the brominated anilines. Winzler and Kelly was able to find such information for BDNA only, for which the U.S. ITC (1979) reported 1978 production of 1.8 x $10^6$ lb. The production level for 1979 was not reported (U.S. ITC, 1980). Hall et al (1980) stated that no information was found in the literature or through industry contacts suggesting that AHB was produced or used commercially in the U.S. In the absence of any data, they suggested that an insignificant quantity of AHB may be produced as a specialty chemical and that a canvassing of the organic chemicals industry would be required to elucidate the situation. AHB's absence from the OPD Directory (OPD, 1980) is strong support for the notion that it is not produced in significant quantities.

Hall et al. (1980) reported that 39 x $10^6$ lb/yr aniline were consumed in the U.S. for manufacturing dyes and intermediates. Because dyes are not considered as a major use for bromine and considering the upper bound on potential bromine-containing aniline-based dyes of 39 x $10^6$ lb/yr, we believe that it is reasonable to assume that actual production of such compounds does not exceed several million pounds per year.

We are aware of no indications that brominated aniline derivatives will experience a rapid growth.

### 2.9.3 Emissions

Hall et al. (1980) stated that no quantitative production and use data were available on which to base emissions estimates. However, they estimated production losses of aniline to be 7 x $10^{-3}$% to air and 2 x $10^{-3}$% to water. Applying these factors to all brominated aniline derivatives and assuming a production rate of such compounds of 5 x $10^6$ lb/yr, we calculated an estimated emission rate of 350 lb/yr to air and 100 lb/yr to water. These rates would be somewhat lower if BDNA were the only derivative produced in notable quantities (1.8 x $10^6$ lb/yr), or much higher if all of the aniline used to produce dyes and intermediates (39 x $10^7$ lb/yr) went to brominated derivatives (which we know is a great exaggeration), in which case we calculated an upper limit on emissions of 2730 lb/yr to air and 780 lb/yr to water. Because aniline is more volatile and is more soluble in water than its brominated derivatives, the actual emission rates would probably be significantly lower than assumed here.

Assuming a 100-percent load factor for a single hypothetical plant that produces all of the upper-limit production of 39 x $10^6$ lb/yr and that emits 7 x $10^{-3}$% of it, we calculated (using the method in Appendix B) a 10-minute concentration at ground level 500 m downwind of 3.8 $\mu g/m^3$, or, assuming that all the airborne material is present as vapors that behave as an ideal gas and that the average molecular weight is 250, 0.37 ppb. If emissions were distributed equally among four locations, the concentration would be 1.0 μg/m$^3$. This worst-case upper-bound estimate indicates that actual emissions of brominated anilines is likely quite low.

We took another, more realistic case for examination. The U.S. ITC (1979) reported that in 1978 1.8 x 10$^6$ lb BDNA were produced by four firms (Table 2.9-2). Assuming that current production is 2 x 10$^6$ lb/yr and that each firm has only one production facility for BDNA, ambient concentrations were calculated as before, the results being that each facility would have a BDNA 10-min average concentration of 0.049 μg/m$^3$ 500 m downwind, which is very low, and the annual average would be substantially lower.

## 2.9.4 Environmental Fate

We found no readily available data on the environmental fate of brominated aniline derivatives. Because they are solids at normal ambient temperatures (Table 2.9-1), they would be expected to be emitted to the air as dust or condensed vapors. In water, they would be expected to concentrate in lipid materials of organisms, based on their high solubility in organic solvents and insolubility in water.

We have found no data on the stability of brominated aniline derivates in the environment. Therefore, we compared information on the biodegradation of aniline and phenol with some of their derivatives. The data presented in Table 2.9-3 illustrate that adding chlorine or a nitro group to the aniline ring or adding bromine or chlorine to phenol (which is structurally similar to aniline) substantially reduces its rate of degradation in various biological systems. This phenomenon may be attributed to increased toxicity or to increased recalcitrance of the derivates. The relatively long time required for degradation of aniline derivatives compared to aniline suggests that the brominated derivatives would tend to accumulate in soil or sediment systems subjected to continuing contamination.

Ambient air concentrations were very crudely estimated in the Environmental Fate section. We found no data on atmospheric stability of even aniline.

## 2.9.5 Health and Ecological Effects

We found no readily available toxicity data for any of the brominated aniline derivatives discussed in this section. Toxic effects of some similar compounds, such as 2-bromo-4-nitroaniline; p-chloroaniline; and aniline hydrochloride demonstrate moderate toxicity in test animals (say 100 mg/kg median lethal dose compared to 3 mg/kg for cyanide) (NIOSH, 1978). Para-chloraniline is mutagenic in the bacterium Escherichia coli, and aniline hydrochloride was carcinogenic in rats in an NCI bioassay (NIOSH, 1979).

Table 2.9-3. Biodegradation of Aniline, Phenol, and Some Derivatives

| | Time for 100% Ring Disruption by Bacteria (h)[a] | | Decomposition Period by a Soil Microflora (d) | Time for Complete Disappearance in Soil Suspension (d) | Degradation in Acclimated Activated Sludge (%) |
|---|---|---|---|---|---|
| | Parent Strain | Mutant | | | |
| Aniline | 54 | 12 | 4 | -- | 94.5 |
| o-chloroaniline | 60 | 18 | >64 | -- | 98.0 |
| m-chloroaniline | 68 | 16 | >64 | -- | 97.2 |
| p-chloroaniline | 59 | 12 | >64 | -- | 96.5 |
| o-,m-,p-nitroaniline | -- | -- | >64 | -- | 0 |
| Phenol | 25 | 8 | 1 | 2 | 98.5 |
| o-bromophenol | 85 | 14 | -- | 14 | -- |
| m-bromophenol | 96 (51%) | 25 | -- | >72 | -- |
| p-bromophenol | 85 (87%) | 22 | -- | 16 | -- |
| o-chlorophenol | 52 | 26 | >64 | 14 | 95.6 |
| m-chlorophenol | 72 | 28 | >72 | >64 | -- |
| p-chlorophenol | 96 | 33 | 16 | 9 | 96.0 |

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[a] For aniline and derivatives, the test system was Aerobacter; 500 mg/l, 30°C.
For phenol and derivatives: Pseudomonas; 200 mg/l; 30°C, except phenol (500 mg/l).

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Source: Verschueren, 1977.

Therefore, in the absence of data to the contrary, the brominated aniline derivatives should be viewed as potential carcinogens. The Interagency Testing Committee designated bromoanilines for testing in April 1979

### 2.9.6 Implications for EPA

Our assessment has not suggested the existence of substantial health threats from brominated aniline derivatives. However, this evaluation is based on very meager data on production and emission rates and toxicology. A reasonable course of action would be to await the results of the toxicological testing recommended by the Interagency Testing Committee (Chem. Engr. News, 11 June 1979, p. 16). Then, further investigation into exposure potential could be focussed on those brominated aniline derivatives, if any, found to be mutagenic, tumorigenic, or teratogenic. Such further study would likely be conducted by EPA's Office of Pesticides and Toxic Substances.

## 2.10 Brominated Benzenes

### 2.10.1 Introduction

Ware and Weast (1977) examined the potential environmental hazards associated with halogenated benzenes. In this section, we summarize their results for brominated benzenes, supplemented with additional information.

Monobromobenzene is used as a solvent in lubricants and fuels, a crystallizing solvent, and a Gignard reagent in organic synthesis. The o- and p-bromochlorobenzenes also form Grignard reagents. Ortho-Dibromobenzene is used as a solvent, as is monobromobenzene, as an ore-flotation fluid, and p-dibromobenzene is used for synthesizing dyes and drugs. Hexabromobenzene was used as a fire-retardant, but it has been replaced by decabromodiphenyl oxide.

The chemical and physical properties of the brominated benzenes are summarized in Table 2.10-1 and the mixed halogenated benzenes in Table 2.10-2. At room temperatures and pressure, brominated benzenes are stable to air, moisture, and light.

### 2.10.2 Production and Consumption

Ware and Weast (1977) found little information on the production or importation of brominated benzenes. Regarding importation, they found that in 1974 222 lb p-bromofluorobenzene were imported and that in 1972 and 1973 7,165 lb and 9,909 lb hexabromobenzene were imported. Considering that imports account for roughly 1% of domestic bromine consumption (Section 2.1), consumption of brominated benzenes in the U.S. may not exceed $10^6$ lb/yr.

## Table 2.10-1. Chemical and Physical Properties of Brominated Benzenes

| Properties | Compounds |  |  |  |  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  | Monobromo-benzene | o-Dibromo-benzene | m-Dibromo-benzene | p-Dibromo-benzene | 1,2,3-Tribromo-benzene | 1,2,4-Tri-bromobenzene | 1,3,5-Tri-bromobenzene | 1,2,3,4-Tetra-bromobenzene | 1,2,3,5-Tetra-bromobenzene | 1,2,4,5-Tetra-bromobenzene | Pentabromo-benzene | Hexabromo-benzene |
| M.P. (°C) | -30.6 | +6.7 | -7 | +87.3 | 88 | 44 | 119 | 47.5 | 98 | 173 | 159 | 326 |
| B.P. (°C) | 156.2 | 225 | 220 | 220 | -- | 275 | 271 | 254 | 329 | -- | Sub. | -- |
| Density (gm/cm$^3$) | 1.4946 | 1.956 | 1.952 | 1.8322 | 2.658 | -- | -- | -- | -- | 3.027 | 3.027 | -- |
| Refractive Index | 1.5597 | 1.6155 | 1.6083 | 1.5742 | -- | -- | -- | -- | -- | -- | -- | -- |
| Solubilities: |  |  |  |  |  |  |  |  |  |  |  |  |
| Water | i | i | i | i | i | i | i | -- | i | i | -- | -- |
| Alcohol | vs | s | s | s | ss | s | ss | -- | s | ss | ss | ss |
| Ether | vs | in | in | vs | vs | vs | s | -- | s | vs | ss | ss |
| Benzene | vs | in | -- | vs | -- | ss | s | -- | s | -- | s | s |
| Chloroform | -- | -- | -- | -- | -- | -- | s | -- | -- | -- | s | s |

in = infinitely soluble
vs = very soluble
s = soluble
ss = slightly soluble
i = insoluble

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Source: Ware and Weast, 1977.

# Table 2.10-2. Chemical and Physical Properties of Mixed Halogenated Benzenes

| Name | Molecular Weight | M.P.(°C) | B.P.(°C) | Den. gm/cm$^3$ | Refractive Index |
|---|---|---|---|---|---|
| 1-Bromo-2-chlorobenzene | 191.46 | -12 | 204 | 1.6382 | 1.5809 |
| 1-Bromo-3-chlorobenzene | 191.46 | -21 | 196 | 1.6302 | 1.5771 |
| 1-Bromo-4-chlorobenzene | 191.46 | 67 | 196 | 1.576 | 1.5531 |
| 1-Bromo-2,3-dichlorobenzene | 225.91 | 60 | 243 | — | — |
| 1-Bromo-3,5-dichlorobenzene | 225.91 | 74 | 232 | — | — |
| 2-Bromo-1,3-dichlorobenzene | 225.91 | 65 | 242 | — | — |
| 2-Bromo-1,4-dichlorobenzene | 225.91 | 32 | 235 | — | — |
| 4-Bromo-1,2-dichlorobenzene | 225.91 | 25 | 237 | — | — |
| 1-Bromo-3-fluorobenzene | 175.01 | — | 151 | — | — |
| 1-Bromo-2-fluorobenzene | 175.01 | — | 57/22mm | — | — |
| 1-Bromo-4-fluorobenzene | 175.01 | -17 | 152 | 1.4946 | 1.5604 |
| 1-Bromo-2-iodobenzene | 282.92 | 2-5 | 257 | 2.2571 | 1.6618 |
| 1-Bromo-3-iodobenzene | 282.92 | -9 | 252 | — | — |
| 1-Bromo-4-iodobenzene | 282.92 | 92 | 251-252 | — | — |

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Source: Ware and Weast, 1974.

In support of the assertion that domestic production and consumption of brominated benzenes is low is the fact that chemical manufacturers reported producing three brominated benzenes in 1978 -- monobromobenzene and pentabromoethylbenzene by Great Lakes Chemical Corp. (West Lafayette, IN) and 2-bromo-1,3,5-triethylbenzene by DuPont (Wilmington, DE). The amounts produced were not disclosed, but the minimum reportable quantity was 5,000 lb (U.S. ITC, 1979). Also, Mara and Lee (1978a) did not list brominated benzene production as one of the significant uses for benzene.

### 2.10.3 Environmental Hazards

Little is known of the carcinogenic or teratogenic potential of the brominated benzenes. Monobromobenzene was reported to be mutagenic in the bacterium Escherichia coli and to be under test at the National Cancer Institute for mammalian carcinogenicity (NIOSH, 1979). Hexachlorobenzene, the chlorinated analog of hexabromobenzene, was reported carcinogenic in hamsters and teratogenic in mice (NIOSH, 1978); therefore, other halogenated benzenes are suspect.

Little is known of the emissions and environmental fate of brominated benzenes (Ware and Weast, 1977). However, the production and consumption rates are thought to be very low, indicating that significant non-occupational exposures are unlikely to occur.

### 2.10.4 Implications for EPA

Brominated benzenes should be suspected of being carcinogenic. However, their rates of production and consumption appear to be sufficiently low to preclude significant non-occupational exposures. Our review suggests that further investigation is not a high priority at this time, but if specific brominated benzenes are found to be carcinogenic, EPA should ensure that no circumstances exist that would allow significant exposure to occur from the presumed low level of production. This would entail, at least initially, identifying and canvassing manufacturers and users.

Bromobenzene has been found in drinking water at low concentrations from chlorination (NRC, 1977), and this is likely a more significant source of exposure than through commercial products. The hazards of halogenated organics in drinking water from chlorination has been under study by EPA and others for several years.

## 2.11 Brominated Alcohols

In a recent study of the potential environmental hazards of halogenated alcohols, two brominated alcohols were examined: 2-bromoethanol and 2,3-dibromo-1-propanol (Lande et al., 1980). The first was reported not to be in commercial use, and 2,3-bibromo-1-propanol was used mainly for making tris(2,3-dibromopropyl) phosphate, an infamous flame retardant that is no longer produced in the U.S. However, 2,3-dibromopropanol was reported as being produced in the U.S. in a quantity exceeding 5,000 lb or $5,000 in value in 1978 (Appendix A) and 1979 (U.S. ITC 1980) by Great Lakes Chemical. This was the only brominated alcohol listed.

Linden et al. (1980) reported that 2,3-dibromo-1-propanol has tested positive in mutagenicity tests, including the *Salmonella typhimurium* test, and that 2-bromoethanol has also proven mutagenic in test systems. Therefore, some brominated alcohols are likely carcinogenic in at least some mammals.

Considering that production and use of brominated alcohols are apparently very low, exposures and risk are likely similarly low. No further investigation by EPA seems warranted at present. However, should specific compounds be determined to be carcinogenic, EPA should verify that exposures are indeed at an acceptably low level by canvassing manufacturers, at least as an initial step.

## 2.12 Tris

Tris, the nickname for tris(2,3-dibromopropyl)phosphate, gained notoriety as a flame retardant in children's sleepwear that was found to be absorbed through the skin of some children wearing treated sleepwear and to be carcinogenic in test mammals. As a result the Consumer Product Safety Commission banned the use of tris in children's clothing (42 Fed. Reg. 18850). Tris was being produced at a level of roughly $10 \times 10^6$ lb/yr, but within a couple of years, other uses were halted voluntarily to avoid product liability, according to the Fire Retardant Chemicals Association (Westport, Conn.). EPA feels that tris is no longer produced or used in the U.S., and it has required that it be notified of domestic production or importation (45 Fed. Reg. 70728, 24 Oct. 1980). As a result, no further action by EPA is warranted.

A significant body of knowledge of tris has arisen within the past few years, including Blackwood et al., 1979a; Blum et al., 1978; and NCI, 1978.

## 2.13 Polybrominated Biphenyls (PBB's)

Between 1970 and 1976, approximately $13 \times 10^6$ lb PBB's were used as fire retardants in synthetic fibers and plastics (Di Carlo et al., 1978). The downfall of PBB's began in 1973 when 500 to 1000 lb Fire Master BP-6 was accidentally mixed into animal feed in place of magnesium oxide. As a result, Michigan Chemical Corp. ceased production in 1974 (Di Carlo et al., 1978).

The bad publicity given PBB's and the fear of liability suits induced manufacturers to cease all production of PBB's. Upon investigation, EPA concluded that production and exposures were nil and that, therefore, regulation under the Toxic Substances Control Act was unwarranted, except to require persons to report the production or importation of PBB's (44 Fed. Reg. 59106, 12 Oct. 1979 and 45 Fed. Reg. 70728, 24 Oct. 1980). In this light, further efforts by EPA are unwarranted.

In addition to the reports cited above, other valuable references for PBB's include Environmental Health Perspectives (EHP), Vol. 23, Apr. 1978 (entire issue devoted to PBB's); EHP, Vol. 24, June 1978 (several papers on PBB's and PCB's); IARC, 1978; Blackwood et al., 1979b; Stratton and Whitlock, 1979; Zweidinger and Pellizzari, 1980; Stratton et al., 1979.

## 2.14 Bromoform

Bromoform is listed by the U.S. ITC under "general antiseptics and antibacterial agents." However, SRI found no indication that bromoform is actually used in those applications, stating that it is thought to be used as a chemical intermediate in the pharmaceuticals industry, in geologic assaying, as an ingredient in fire-resistant chemicals and gauge fluids, as a solvent for waxes, greases, and oils, and as an intermediate in organic synthesis (Urso, et al., 1978). NAS (1978) reported bromoform's 1975 production rate to be under $1.1 \times 10^6$ lb and its end use to be for chemical intermediates. Only Dow Chemical Co. is listed as a producer in 1979 by the U.S. ITC, implying that Dow was the only firm to produce over 1,000 lb or over $1,000 worth of bromoform (U.S. ITC, 1980).

Urso et al. (1978) concluded that, because the market for bromoform is small and specialized, rapid growth was unlikely. We have found nothing in the recent literature to indicate the contrary.

Bromoform is a heavy volatile liquid, with a freezing point of 8.3°C and a vapor pressure of 10 mm Hg at 34°C. It is slightly soluble in water (0.3 g/100 g water at 15°C) but soluble in many organic liquids (NAS, 1978).

In a review of bromoform's toxicology, NAS (1978) concluded that little is known. It is regarded as being highly toxic, though less so than chloroform, and mutagenicity in bacteria has been reported (NAS, 1978). Intraperitoneal administration in mice has reportedly caused tumors, and bromoform is being tested by NCI for animal carcinogenicity (NIOSH, 1979). OSHA's 8-hr time-weighted average limit is 0.5 ppm (NIOSH/OSHA, 1978).

While very little is known with much certainty regarding the exposure potential for bromoform, the information that we do have -- in particular, an apparently low rate of production and its use as a chemical intermediate -- indicates that exposure is likely very low. In a survey of chlorinated drinking waters, no bromoform was detected, but the mixed haloforms bromodichloromethane and dibromochloromethane were, in addition to chloroform, carbon tetrachloride and methylene chloride (NAS, 1978).

Some marine algae have a very high bromoform content; for example, 1% (dry weight) in the red seaweed Asparagopsis (Josephson, 1977). We have found no measurements of bromoform in seawater.

If bromoform turns out positive in NCI's carcinogenesis test, further investigation into its exposure potential might be warranted. This would entail firmer identification of production rates and processes and use patterns. From such information, a reasonable estimate of emissions and exposure rates could be made.

## 2.15 Miscellaneous Brominated Hydrocarbons

### 2.15.1 Acetylene Tetrabromide ($Br_2CHCHBr_2$)

In a toxicological evaluation of chemicals proposed for use as heat-transfer fluids for solar heating and cooling, only one brominated compound was considered: acetylene tetrabromide (1,1,2,2-tetrabromoethane). Of the 34 liquids examined, acetylene tetrabromide was the third most toxic and was therefore not recommended as an option (Buchan, 1976). Its established occupational limit is 1 ppm (NIOSH/OSHA, 1978).

Hawley (1977) lists the following uses for acetylene tetrabromide: separating minerals by specific gravity; solvent for fats, oils, and waxes; fluid in liquid gauges; and solvent in microscopy. Dow Chemical Co. is listed as the only producer in 1979 (U.S. ITC, 1980). Its listing implies that at least 5,000 lb or $5,000 worth of acetylene tetrabromide were produced.

We have found no indications that the use pattern or production and consumption rates of acetylene tetrabromide will change substantially in the future, especially considering its high toxicity.

### 2.15.2 Bromotrifluoromethane ($BrCF_3$)

In a review of the environmental hazards associated with the use of major quantities of saturated one- and two-carbon chlorinated and brominated fluorocarbons, only one brominated compound was considered: bromotrifluoromethane (fluorocarbon 1301). It was reported that the 1972 production level of bromotrifluoromethane was roughly $4 \times 10^6$ lb, 95% being used as a fire-extinguishing agent and 5% as a refrigerant, with production capacity reportedly increasing by $10 \times 10^6$ lb/yr in 1975. DuPont was thought to be the only manufacturer (Howard et al., 1974). The U.S. ITC listed one unidentified producer in 1978 and 1979 (U.S. ITC, 1979 and 1980), and duPont is indeed reportedly it (Chem. Engr. News, 8 Dec., 1980, p. 86).

Bromotrifluoromethane has low toxicity, its occupational limit being 1000 ppm (NIOSH, 1978). The greatest environmental hazard from brominated hydrocarbons may be stratospheric ozone depletion (see discussion in Section 2.3.4).

An Israeli-developed fire-extinguishing system for military vehicles is being adapted for use in domestic military and perhaps commercial applications (Chem. Engr. News, 8 Dec. 1980, p. 86). The market potential has not been reported, but it could be large if such a system became standard equipment on private motor vehicles and airplanes. Also, EPA is preparing to regulate several chlorofluorocarbons (45 Fed. Reg. 66726, 7 Oct. 1980), some of which are used as fire-extinguishing agents and refrigerants (Hawley, 1977). To the extent that bromotrifluoromethane or other brominated fluorocarbons could substitute for chlorofluorocarbons, increased production of the former could result. However, EPA had earlier suggested regulating brominated fluorocarbons and chlorofluorocarbons (Chem. Week 12 Jan. 1977, p. 22), indicating that EPA is aware of the hazard potential of the brominated compounds and that it might act against large-scale substitutions.

### 2.15.3 Ethyl Bromide

Ethyl bromide is reportedly used mainly as an ethylating agent for pharmaceutical manufacture. Other uses include refrigerant, solvent, and local anesthetic. Production level was last reported for year 1969: $1.25 \times 10^6$ lb (SRI, 1980). We found no indication of dramatic changes in the level of production or consumption of ethyl bromide. It has been selected for NCI carcinogenesis testing (NIOSH, 1978). If carcinogenic, an exposure assessment may be warranted.

### 2.15.4 Others

NAS (1978) listed methylene bromide (dibromomethane) and carbon tetrabromide as chemical intermediates, with bromodichloromethane and dibromochloromethane as research chemicals. No production data for these chemicals are available, but production levels are likely quite low. Considering that chloroform and carbon tetrachloride are considered by many to be animal carcinogens, these similar brominated compounds might also be found to be carcinogenic. If so, exposure assessments may be warranted. The mixed bromochloromethanes have been found in chlorinated drinking waters (NAS, 1978).

## 2.16 Thallium Bromide Optical Fibers

New optical fibers containing thallium bromide have been developed recently in Japan. One type is composed of thallium bromide and thallium iodide, and it was developed to carry infrared light for long-distance communications without relays. The optical fiber may also have immediate uses in medical and industrial lasers and is said to have a high market potential (Japanese Economic Journ., 27 June 1980, p. 9). A second type of new optical fiber is composed of thallium bromide and thallium iodide. It transmits carbon dioxide laser light of 20 watts and is said to have wide applicability (Japanese Economic Journ., 22 Jan. 1980, p. 13).

Thallium bromide is highly toxic, the lowest published lethal dose being 29 mg/kg by subcutaneous administration in mice (NIOSH, 1978). Thallium bromide, being nonvolatile (melting point is 460°C [Hawley, 1977]) and being bound in the optical fiber during fabrication, should have a low exposure potential during use, except perhaps for the actual handling of the fibers. Another potential avenue of exposure is in the disposal of the discarded fibers. The potential for thallium bromide leaching from land-filled fibers to water supplies or dispersing from incinerated fibers to the atmosphere is unknown. A further market and environmental assessment for thallium bromide-containing optical fibers may be warranted.

## 2.17 Lithium Bromide Refrigerant

Lithium bromide is used as an absorbent in the water/LiBr absorption-cycle refrigeration process. Water/LiBr has been the most common absorption cycle system in both conventional and solar applications (Nash and Harstad, 1976). However, the use of LiBr in air conditioning has reportedly declined somewhat (Singleton, 1979). Reports of major installations of water/LiBr systems and reports of research directed toward improving LiBr-based absorption systems appear in the recent literature. However, we have no indications that a substantial increase in the growth rate of such uses is impending. The Bureau of Mines forecasts a low rate of increase comparable to the growth of Gross National Product (Singleton, 1979).

The demand for lithium in air conditioning was roughly $4 \times 10^5$ lb/yr from 1968 to 1977 (U.S. Bur. Mines, 1979). This translates to $5 \times 10^6$ lb LiBr and $4.6 \times 10^6$ lb contained bromine.

The use of lithium bromide in refrigeration systems presents little opportunity for human exposure, and LiBr is of low toxicity (Hawley, 1977; NIOSH, 1978).

## 2.18 Hydrogen Production

Research is underway to develop an efficient method for producing hydrogen gas for use as a fuel and as an industrial chemical. Both thermochemical and electrolytic processes are being studied. One of the processes -- a thermochemical/electrolytic hybrid system -- utilizes bromine as a major reactant. This "sulfuric acid/hydrogen bromide cycle" is comparable in estimated efficiency and cost to others, although it may take 10 to 15 years to complete the research necessary to determine which is clearly the superior process (Cox, 1978). If a process utilizing bromine becomes favored, a new demand for bromine would occur. However, the bromine being recycled in the system would limit the demand and exposure potential.

This application of bromine presents no greater hazard than bromine itself. No further consideration by EPA is recommended.

### 2.19 Brominated Butyl Rubber

Exxon Chemical Co. is reportedly planning to modify its butyl rubber plant at Baton Rouge, Louisiana to produce bromobutyl (Journal of Commerce, 17 June 1980, p. 8). SRI (1980) reported that halobutyl rubber consumption has increased rapidly during the last decade, but no indication was given of demand for either bromobutyl or chlorobutyl. Halobutyl rubbers are used as inner liners for tubeless tires, white sidewall tires, non-toxic food containers and jar seals (zinc oxide cure), blends with highly unsaturated rubbers to improve heat and ozone resistance, and adhesive layers (Codd, et al., 1972).

Bromobutyl is produced by the bromination of butyl rubber (Codd et al., 1972), so brominated intermediate chemicals are not involved.

Codd et al. (1972) reported BF Goodrich Chemical Company as the only domestic producer of bromobutyl, called Hycar 2202.

### 2.20 Dodecyl Trimethyl Ammonium Bromide (DTAB)

DTAB is a cationic surfactant used for enhancing oil recovery in tertiary recovery operations (Chemtech, June 1980, p. 356). No information on quantities used is available. As the price of oil has increased, the use of DTAB has likely increased in step as tertiary recovery was pursued.

The use of DTAB in oil reservoirs may not cause environmental problems because oil reservoirs are relatively well isolated from the biosphere. However, risks associated with producing and transporting DTAB will increase as its use increases. We have found no information on the toxicity of DTAB.

Further investigation into the market trends and associated environmental effects of DTAB is advisable at this time, as its demand could be growing rapidly.

### 2.21 Zinc-Bromine Batteries

Zinc-bromine batteries have potential applications in electric power storage by utilities (Gould, 1979) and in electric cars (Mock, 1979). Such applications should pose no significant environmental problems from the bromine portion of the product. During product disposal (landfill, for example), any elemental bromine remaining should rapidly oxidize to bromide ion upon contact with soil and refuse, and bromide ion is no more toxic than is chloride.

## 2.22 Bromosilanes in Silicon Production

Promising research has been reported on producing solar-energy grade silicon from bromosilanes (Schumacher et al., 1979). If this technology were used to produce the solar collectors of the future, a large market could result. Because this will likely not occur for many years, now may be an opportune time to further assess the market potential and associated environmental effects of this technology.

## 3.0 INFORMATION DEFICIENCIES AND REMEDIES

Many gaps exist in the information available on the bromine-based chemicals industry. Where necessary, we made assumptions allowing us to at least tentatively bridge the gaps. In most cases, our analyses indicate that filling the data gaps should not be a high priority in light of other pressing issues that EPA faces. However, as noted in parts of Section 2.0, several issues do require further attention:

- Better definition of the brominated flame retardants industry and associated environmental effects is needed. A current EPA-sponsored study strives to achieve this goal (Section 2.4.4).
- The effect of methyl bromide on stratospheric ozone deserves greater attention (Section 2.3.10).
- The lack of carcinogenicity and food-residue data for methyl bromide may hamper EPA's planned review under the Federal Insecticide, Fungicide, and Rodenticide Act (Section 2.3.10).
- Additional research into the environmental effects of bromine chloride utilization would be useful to further substantiate the evidence that bromochlorination is less environmentally damaging than chlorination (Section 2.6.7).
- Better characterization of potential environmental effects of calcium bromide drilling fluid (Section 2.5.3) and DTAB, a brominated surfactant used in tertiary oil recovery (Section 2.20) may be warranted. Considering that drilling activities have expanded substantially in recent years, a review of current petroleum drilling and production technologies would be useful and timely.
- Because vinyl bromide is carcinogenic in test animals, a detailed risk assessment would be appropriate (Section 2.7.10).
- Further market and environmental assessment for thallium bromide optical fibers would be appropriate exploratory research (Section 2.16).
- Further market and environmental assessment for bromosilanes may be advisable (Section 2.22).

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# APPENDIX A

## Brominated Organic Chemicals Listed by the International Trade Commission as being Manufactured in the U.S. during 1978

# Brominated Organic Chemicals Listed by the International Trade Commission as being Manufactured in the U.S. during 1978[1]

## Cyclic Intermediates

1. 1-Amino-4-bromo-9,10-dihydro-9, 10-dioxo-2-anthracenesulfonic acid and sodium salt   TRC, VPC
2. *1-Amino-2-bromo-4-hydroxyanthraquinone   AC, DUP, GAF, VPC
3. 1-Amino-2-bromo-4-p-toluidinoanthraquinone   TRC
4. 1-Amino-2,4-dibromoanthraquinone   DUP, TRC, VPC
5. 1,2-Bis(tribromophenoxy)ethane   VEL
6. p-Bromoaniline   EK
7. p-Bromoanisole   OPC
8. 3-Bromo-7H-benz[de]anthracen-7-one (3-Bromobenzanthrone)   ACY
9. Bromobenzene,mono   GTL
10. 2-Bromo-6-chloro-4-nitroaniline   HST
11. 4-Bromo-3,5-dihydroxybenzamide   PCW
12. *2-Bromo-4,6-dinitroaniline   AC, GAF, HST, SDC
13. Bromoethylbenzene   RSA
14. 2-Bromo-4'-nitroacetophenone   RSA
15. -Bromo-p-nitrotoluene (p-Nitrobenzyl bromide)   DUP
16. (p-Bromophenyl)acetonitrile   SFS
17. 2-Bromopyridine   RIL
18. 4-Bromoresorcylic acid   PCW
19. 4-Bromoresorcylic acid, ethanolamide   PCW
20. 4-Bromoresorcylic acid, methyl ester   PCW
21. 8-Bromotheophyline   CHT
22. o-Bromotoluene   RSA
23. p-Bromotoluene   SFS
24. 2-Bromo-1,3,5-triethylbenzene   DUP

## Cyclic Intermediates
(continued)

25. 4,10-Dibromo-anthantrone VPC

26. 3,9-Dibromo-7H-benz[de]anthracen-7-one TRC

27. 4,4'-Dibromobiphenyl EK

28. 2,6-Dibromo-4-nitroaniline HST, SDC

29. 2,6-Dibromo-4-nitrophenol SW

30. 3,5-Dibromo-3'-trifluoromethylsalicylanilide (Fluorophene) PCW

31. Pentabromochlorocyclohexane DOW

32. Pentabromoethylbenzene GTL

33. 3,3',5,5'-Tetrabromo-m-cresolsulfonphthalein, sodium salt EK

34. Tetrabromophthalic anhydride VEL

35. 2,4,6-Tribromophenol VEL

36. 3,4',5-Tribromosalicylanilide PCW

## Medicinal Chemicals

37. Bromodiphenhydramine hydrochloride PD

38. Brompheniramine maleate HEX, SCH

39. Bromoform DOW

40. Camphor, monobromated PEN

41. Homatropine hydrobromide ARA

42. Homatropine methylbromide ARA

43. Neostigmine bromide HEX

44. Neostigmine methylsulfate HOF

45. Pyridostigmine bromide HOF

46. Dextromethorphan hydrobromide HOF

## Pesticides and Related Products

47. 2-Bromo-4'-hydroxyacetophenone BKM

48. 5-Bromo-3-sec-butyl-6-methyluracil (Bromocil) DUP

49. 3,5-Dibromo-4-hydroxybenzonitrile, octanic acid esters (Bromoxynil octanoate) RDA

50. O-(4-Bromo-2,5-dichlorophenyl)O-methylphenylphosphonothioate (Leptophos) VEL

51. 4-Bromoacetoxymethyl-N-dioxoline EFH

52. 1,2-Dibromo-2,2-dichloroethyl dimethyl phosphate (Naled) SHC

53. 1,2-Dibromo-3-chloropropane (DBCP) DOW

54. Methyl Bromide (Bromomethane) DOW, GTL, VEL

## Miscellaneous End-Use Chemicals and Chemical Products

55. *Ethylene dibromide DOW, PPG, TNA

## Miscellaneous Cyclic and Acyclic Chemicals

56. N-Bromoacetamide ARA

57. Bromochloromethane DOW

58. Bromoethane (Ethyl bromide) DOW, GTL, VEL

59. 1-Bromopentane (n-Amyl bromide) HMY, WCC

60. Bromotrichloromethane VEL

61. Dibromomethane (methylene bromide) DOW

62. 1,1,2,2-Tetrabromoethane (Acetylene tetrabromide) DOW

63. Vinyl bromide (Bromoethylene) TNA

64. Brominated (Including bromochlorinated) hydrocarbons, all other GTL, HMY, OMC, VEL, WCC

65. 2-Bromobutane (sec-Butyl bromide) VEL

66. Bromochloromethane DOW

67. 1-Bromo-3-chloropropane (Trimethylenechlorobromide) VEL

68. Bromoethane (Ethyl bromide) DOW, GTL, VEL

69. 1-Bromohexane (n-Hexyl bromide) WCC

70. 1-Bromo-octadecane HMY

## Miscellaneous Cyclic and Acyclic Chemicals
(continued)

71. 2-Bromo-2-chloro-1,1,1 trifluoroethane ICI

72. Bromotrifluoromethane X

73. Dibromodifluromethane X

74. 1,2-Dibromo-1,1,2,2-tetrafluoroethane X

75. 2,3-Dibromopropanol GTL

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[1] Source: U.S. ITC, 1979. Compounds for which production or sales exceeded 5,000 lb or $5,000 (1,000 lb or $1,000 for medicinals) were reported. Compounds marked by an asterisk are the only ones for which the production volume was reported. The manufacturer identification codes following each entry are defined below:

| | |
|---|---|
| AC | American Color and Chemical Corp., Greenwich, CT |
| ACY | American Cyanamid Co., Wayne, NJ |
| ARA | Arapahoe Chemicals, Inc., Sub/Sytnex U.S.A. Inc., Boulder, CO |
| BKM | Buckman Laboratories, Inc., Memphis, TN |
| CHT | Chattem, Inc., Chattanooga, TN |
| DOW | Dow Chemical Co., Midland, MI |
| DUP | E.I. duPont de Nemours and Co., Inc., Wilmington, DE |
| EFH | E.F. Houghton and Co., Philadelphia, PA |
| EK | Eastman Kodak Co., Rochester, NY |
| GAF | GAF Corp., Chattanooga, TN and Linden, NJ |
| GTL | Great Lakes Chemical Corp., West Lafayette, IN |
| HEX | Hexagon Laboratories, Inc., Bronx, NY |
| HMY | Humphrey Chemical Co., North Haven, CT |
| HOF | Hoffman-La Roche, Inc., Nutley, NJ |
| HST | American Hoechst Corp., Reading, PA |
| ICI | ICI Americas, Inc., Wilmington, DE |

| | |
|---|---|
| OMC | Olin Corp., Stamford, CT |
| OPC | Orbis Products Corp., Hanover, NJ |
| PCW | Pfister Chemical, Inc., Ridgefield, NJ |
| PD | Parke, Davis and Co., Sub of Warner-Lambert Co., Detroit, MI |
| PEN | Penick Corp., Lyndhurst, NJ |
| PPG | PPG Industries, Inc., Pittsburgh, PA |
| RDA | Rhone-Poulenc, Inc., New Brunswick, NJ |
| RIL | Railly Tar and Chemical Corp., Indianapolis, IN |
| RSA | RSA Corp., Ardsleg, NY |
| SCH | Schering Corp., Union, NJ |
| SDC | Martin-Marietta Corp., Sodyeco Div., Charlotte, NC |
| SFS | Stauffer Chemical Co., Specialty Div., San Francisco, CA |
| SW | Sherwin-Williams Co., Cleveland, OH |
| TNA | Ethyl Corp., Richmond, VA |
| TRC | Toms River Chemical Corp., Toms River, NJ |
| VEL | Vesicol Chemical Corp., Chicago, IL |
| VPC | Mobay Chemical Corp., Venona Dyestuff Div., Union, NJ |
| WCC | White Chemical Corp., Bayonne, NJ |
| X | Not identified |

# APPENDIX B

# Air Pollutant Dispersion Calculation

# Air Pollutant Dispersion Calculation

In lieu of a very extensive monitoring program, modeling is essential for accurately estimating population exposures and risk from air pollutants. However, a detailed modeling approach (based on well-characterized meteorology, terrain, turbulence in the wake of the building, and the like) was beyond the scope of this study. Instead, we used a simple approach to estimate the semi-worst-case concentrations of pollutant downwind at ground level. Our approach is a combination of those used by Mitre Corporation and by GCA Corporation on previous EPA studies (see for example, Johns, 1976 and Patterson et al., 1976).

The downwind 10-minute concentrations at ground level from a point source can be predicted by the Gaussian plume equation (Turner, 1970):

$$\chi = \frac{Q}{\pi u \sigma_y \sigma_z} \exp \left[ -0.5 \frac{H}{\sigma_z} \right]^2 , \qquad \text{(Eqn B-1)}$$

where:
$\chi$ = downwind concentration (grams/$m^3$)
$Q$ = uniform emission rate (grams/sec)
$u$ = mean wind speed affecting the plume (meters/sec)
$H$ = effective stack height; that is, sum of stack height plus plume rise (meters)
$\sigma_y$ = horizontal dispersion coefficient evaluated in terms of downwind distance to the point for which the concentration is being computed (meters)
$\sigma_z$ = vertical dispersion coefficient evaluated in terms of downwind distance to the point for which the concentration is being computed (meters)

Assuming the source to be an area source 100 meters on a side, the virtual point source upwind of the actual area source has a horizontal dispersion coefficient ($\sigma_{yo}$) equal to 100 meter/4.3 = 23.3 meters, which translates to the virtual point source being approximately 310 meters upwind from the actual area source (assuming Stability Class D, neutral stability).

Assuming further that:

1) the pollutant is non-reactive,
2) the average effective stack height is 10 meters,
3) the average wind speed is 2 meters per second,
4) neutral stability conditions (Class D),
5) the point of interest is 500 meters downwind from the plant,

Equation B-1 reduces to:

$$\chi = \frac{Q}{(3.14)(2\ \text{m/sec})(56\ \text{m})(27\ \text{m})} \exp\left[-0.5\ \left(\frac{10\text{m}}{27\text{m}}\right)\right]^2$$

$$\chi = \frac{Q}{9495}\ (0.93)\ (\text{grams/m}^3) \qquad \text{(Eqn B-2)}$$

$$\chi = 9.8 \times 10^{-5} Q$$

At 100 m from the plant,

$$\chi = 2.7 \times 10^{-4} Q \qquad \text{(Eqn B-3)}$$

For example, assuming a plant downtime of five days per year and an emission rate equal to one percent of the production rate, a plant producing 100 million pounds of a substance per year would emit 15 grams per second of pollutant, resulting in a ground level concentration 500 meters downwind from the plant of 1.5 mg per $m^3$.

# APPENDIX C

## Listing of Bromine-Base Fire Retardants[1]

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[1] Obtained from:

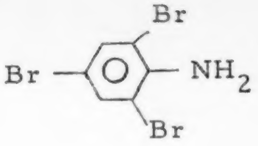
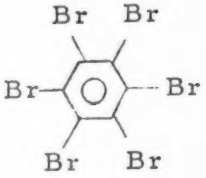
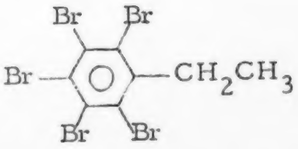
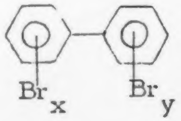
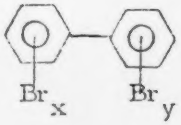
Mr. Roman W. Kuchkuda, Project Officer
Chemical Hazard Identification Branch
Assessment Division
Office of Pesticides & Toxic Substances
U.S. Environmental Protection Agency
Washington, D.C.

# BROMINE BASED FIRE RETARDANTS

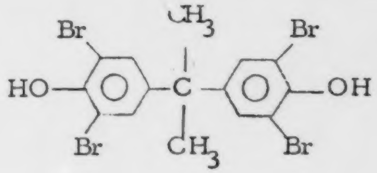
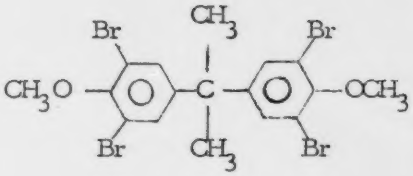
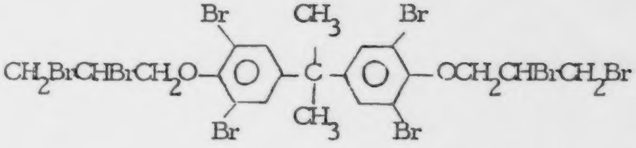
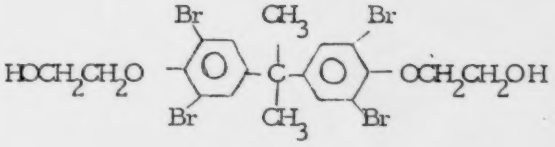
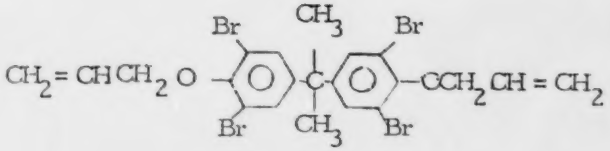
Department of Chemistry
Polytechnic Institute of New York
333 Jay Street
Brooklyn, New York 11201

## Table 1a. Bromine Based Fire Retardant

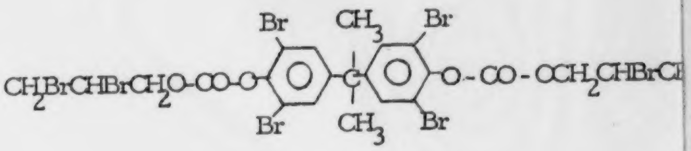
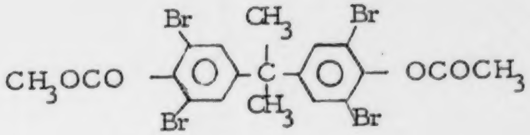
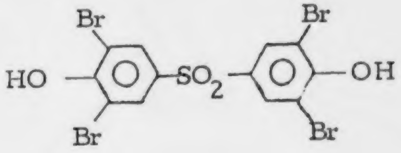
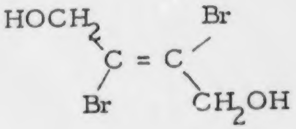
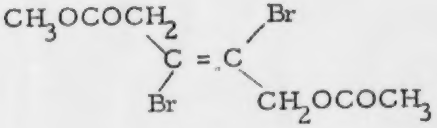
(Known Structures)

| Fire Retardant | Chemical Name | Chemical Structure |
|---|---|---|
| Acrylate, 2, 3-dibromopropyl- | 2, 3-dibromopropyl propenoate | $CH_2=CH-CO-OCH_2CHBrCH_2Br$ |
| Ammonium bromide | ammonium bromide | $NH_4Br$ |
| Aniline, 2, 4, 6-tribromo- | 2, 4, 6-tribromoaniline |  |
| Benzene, hexabromo- | hexabromobenzene |  |
| Benzene, pentabromoethyl- | 1-ethyl-2, 3, 4, 5, 6-pentabromobenzene |  |
| Biphenyl, hexabromo- | - - - - |  x+y=6 |
| Biphenyl, octabromo- | - - - - |  x+y=8 |

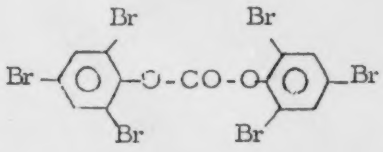
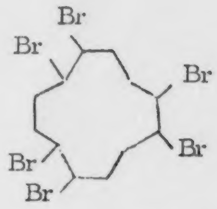
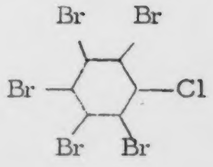
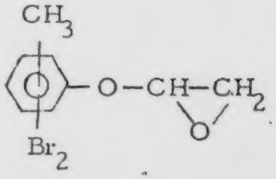
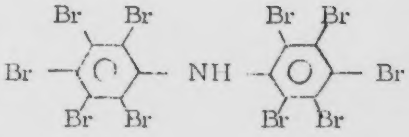
| Trade Name | Manufacturer/ Supplier(1) | Recommended Use(2) |
|---|---|---|
| Great Lakes AE-59 | GL | AC, EP, PAN, PES, PO, PS |
| - - | DOW | CA, PS, PUR |
| Great Lakes AN-73 | GL | ABS, EP, PMMA, PS |
| Great Lakes BZ-87 | GL | ABS, PMMA, PP, PS |
| Great Lakes EB-80<br>Great Lakes EB-80P<br>HFO-105 | GL<br>GL<br>HEX | ABS, AC, EP, PES, PMMA, PP, PS, PUR |
| Great Lakes BP-76 | GL | ABS, EP, PC, PE, PES, PP, PS, PUR |
| - - | GL | ABS, EP, PC, PE, PES, PP, PS, PUR |

| Fire Retardant | Chemical Name | Chemical Structure |
|---|---|---|
| Bisphenol A, tetrabromo- | 4,4'-isopropylidenebis (2,6-dibromophenol) |  |
| Bisphenol A, tetrabromo-, bis(methyl- -ether) - | isopropylidenebis (4-methoxy-3,5-dibromophenyl) |  |
| Bisphenol A, tetrabromo-, bis(2,3- -dibromopropyl ether)- | isopropylidenebis (2',3,3',5-tetrabromo-4-phenyl propyl ether) |  |
| Bisphenol A, tetrabromo-, bis(2- -hydroxyethyl ether)- | isopropylidenebis (2-hydroxy-3',5'-dibromo-ethyl 4-phenyl-ether) |  |
| Bisphenol A, tetrabromo-, bis(allyl-ether) - | isopropylidenebis (3',5'-dibromo-allyl 4-phenyl ether) |  |

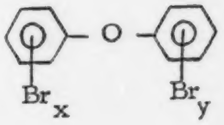
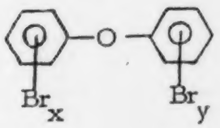
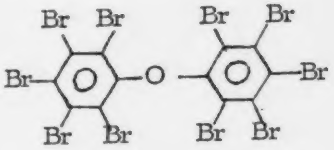
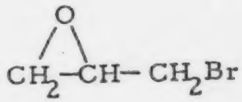
| Trade Name | Manufacturer/ Supplier[1] | Recommended Use[2] |
|---|---|---|
| Great Lakes BA-59 | GL | ABS, EP, PC, PES, PMMA, PP, PS, PUR |
| Great Lakes BA-59P | GL | |
| - - | DOW | |
| FireMaster BP4A | VEL | |
| - - | GL | ABS, PMMA, PP, PS |
| - - | GL | ABS, PMMA, PP, PS |
| Great Lakes BA-50 | GL | ABS, EP, PES, PUR |
| Great Lakes BA-50P | GL | |
| - - | GL | ABS, PES, PS |

| Fire Retardant | Chemical Name | Chemical Structure |
|---|---|---|
| Bisphenol A, tetrabromo-, bis(2, 3- -dibromopropyl carbonate)- | isopropylidenebis (2', 3, 3', 5'-tetrabromo-4-phenyl propyl carbonate) |  |
| Bisphenol A, tetrabromo-, diacetate- | isopropylidenebis (3,5-dibromo- 4-phenyl acetate) |  |
| Bisphenol S, tetrabromo- | 4, 4', -dihydroxy-3, 3', 5, 5'-tetrabromo-diphenyl-sulfone |  |
| Butenediol, dibromo- | trans-2, 3-dibromo-2-butene-1,4-diol |  |
| Butenediol, dibromo-, diacetate- | trans-2, 3-dibromo-2-butene-1, 4-diacetate |  |

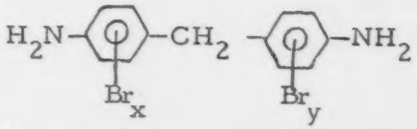
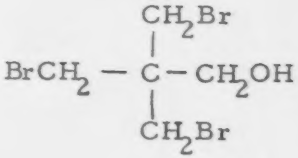
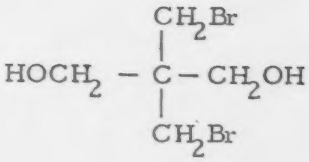
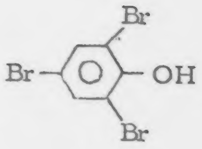
| Trade Name | Manufacturer/ Suppier(1) | Recommended Use(2) |
|---|---|---|
| - - | GL | ABS, PMMA, PP, PS |
| - - | GL | ABS, PMMA, PP, PS |
| - - | GL | ABS, PMMA, PP, PS |
| - - | GAF | ABS, EP, PES, PETH, PS, PUR |
| - - | GAF | ABS, PES, PS, PUR |

| Fire Retardant | Chemical Name | Chemical Structure |
|---|---|---|
| Carbonate, bis(2,4,6-tribromo-phenyl)- | bis(2,4,6-tribromophenyl) carbonate |  |
| Cyclododecane, hexabromo- | 1,2,5,6,9,10-cyclododecane |  |
| Cyclohexane, pentabromochloro- | chloropentabromocyclohexane |  |
| Cresol, dibromo-, glycidyl ether- | - - - - |  |
| Diphenyl amine, decabromo- | decabromo-diphenyl amine |  |

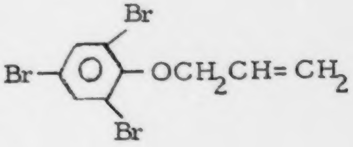
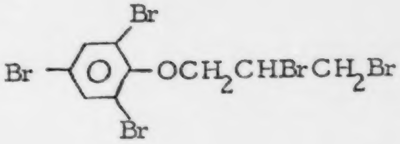
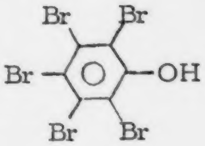
| Trade Name | Manufacturer/ Suppliers(1) | Recommended Use(2) |
|---|---|---|
| Great Lakes BC-70 | GL | ABS, PMMA, PP, PS |
| Great Lakes CD-75 | GL | ABS, PMMA, PP, PS |
| FR-651-A | DOW | ABS, PS, R |
| Great Lakes CG-49 | GL | EP |
| - - | GL | ABS, PP, PS |

| Fire Retardant | Chemical Name | Chemical Structure |
|---|---|---|
| Diphenyl oxide, pentabromo- | - - - - |  x+y = 5 |
| Diphenyl oxide, octabromo- | - - - - |  x+y = 8 |
| Diphenyl oxide, decabromo- | decabromo-diphenyl ether |  |
| Epibromohydrin | 1-bromo-2, 3-epoxy-propane |  $CH_2-CH-CH_2Br$ |
| Methacrylate, 2, 3-dibromopropyl | 2,3-dirbomopropyl-<br>2-methylpropenoate | $CH_2=C(CH_3)-CO-OCH_2CHBrCH_2Br$ |
| Methane, bromotrichloro- | bromotrichloromethane | $BrCCl_3$ |

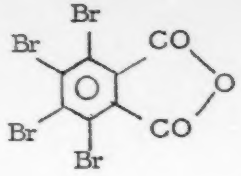
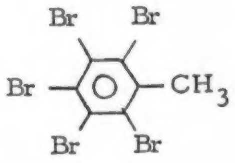
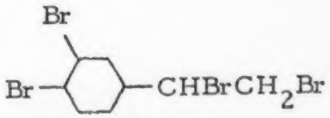
| Trade Name | Manufacturer/ Supplier[1] | Recommended Use[2] |
|---|---|---|
| Great Lakes DE-71 | GL | EP, PES, PH, PO, PUR, PVC |
| Great Lakes DE-79<br>Great Lakes FR-143 | GL<br>GL | ABS, EP, PES, PO, PS, PUR |
| Great Lakes DE-83<br>Great Lakes DE-83P<br>Great Lakes DE-83R<br>FR-300-BA<br>HFO-102 | GL<br>GL<br>GL<br>DOW<br>HEX | ABS, EP, N, PAN, PC, PE, PES, PH, PO, PP, PS, PUR, PVC |
| Great Lakes EBH | GL | PUR |
| Great Lakes ME-56 | GL | AC, EP, PAN, PES, PO, PS |
| - - | MIC | EP |

| Fire Retardant | Chemical Name | Chemical Structure |
|---|---|---|
| Methylenedianinile, tetrabromo- | - - - - |  x+y= 4 |
| Neopentyl alcohol, tribromo- | 2, 2-bis(bromomethyl)<br>3-bromo-1-propanol |  $\begin{array}{c} \mathrm{CH_2Br} \\ \vert \\ \mathrm{BrCH_2 - C - CH_2OH} \\ \vert \\ \mathrm{CH_2Br} \end{array}$ |
| Neopentyl glycol, dibromo- | 2, 2-bis(bromomethyl)-<br>1, 3-propanediol |  $\begin{array}{c} \mathrm{CH_2Br} \\ \vert \\ \mathrm{HOCH_2 - C - CH_2OH} \\ \vert \\ \mathrm{CH_2Br} \end{array}$ |
| Neopentyl glycol, dirbromo-, polyester of-maleic and o-phthalic acids- | - - | - - - - |
| Phenol, 2, 4, 6-tribromo- | 2, 4, 6-tribromophenol |  |

| Trade Name | Manufacturer/ Supplier$^{(1)}$ | Recommended Use$^{(2)}$ |
|---|---|---|
| - - | GL | ABS, EP, PMMA, PS |
| FR-1360<br>FR-2249 | DOW<br>DOW | PUR |
| FR-1138 | DOW | EP, PES, PUR |
| FR-1540 | DOW | PES |
| Great Lakes PH-73<br>FR-100-BA | GL<br>DOW | ABS, EP, PH, PS |

| Fire Retardant | Chemical Name | Chemical Structure |
|---|---|---|
| Phenol, 2,4,6-tribromo-, allyl ether- | 2', 4', 6'-tribromo-allyl phenyl ether |  |
| Phenol, 2,4,6-tribromo-, 2,3-dibromo-propyl ether - | 2,2', 3', 4,6-pentabromo-phenyl propyl ether |  |
| Phenol, pentabromo- | pentrabromophenol |  |
| Phosphate, tris(2,3-dibromopropyl)- | tris(2,3-dibromopropyl) phosphate | $(CH_2BrCHBrCH_2O)_3PO$ |
| Phosphonium bromide, ethylenebis--tris(2-cyanoethyl)- | ethylene bis [tris(2-cyanoethyl)--phosphonium bromide] | $(NCCH_2CH_2)_3\overset{+}{P}CH_2CH_2\overset{+}{P}(CH_2CH_2CN)_3 2\overline{Br}$ |
| Phosphonium bromide, tetrakis--(2-cyanoethyl)- | tetrakis (2-cyanoethyl) phosphonium--bromide | $(NCCH_2CH_2)_3\overset{+}{P}\overset{-}{Br}$ |

| Trade Name | Manufacturer/ Supplier[1] | Recommended Use[2] |
|---|---|---|
| - - | GL | ABS, PES, PS |
| - - | GL | ABS, PMMA, PP, PS |
| Great Lakes PH-82 | GL | EP, PH |
| Great Lakes TP-69 | GL | ABS, AC, CA, CN, EP, PES, PH, PMMA, PS, PUR, PVC |
| FR-2406 | DOW | |
| Fyrol HB-32 | ST | |
| Fyrol 32B | ST | |
| FireMaster T23P | MIC | |
| LV-T23P | MIC | |
| CYAGARD RF-1 | AC | PE, PP, PS, R |
| CYAGARD RF-272 | AC | PE, PP, PS |

| Fire Retardant | Chemical Name | Chemical Structure |
|---|---|---|
| Phtalic anhydride, tetrabromo- | tetrabromophtalic anhydride |  |
| Propanol, 2, 3-dibromo | 2, 3-dibromo-1-propanol | $CH_2BrCHBrCH_2OH$ |
| Toluene, pentabromo- | 2,3,4,5,6-pentabromotoluene |  |
| Vinyl bromide | bromoethene | $CH_2 = CH-Br$ |
| Vinylcyclohexene, tetrabromo- | 1-(1,2-dibromoethyl)-<br>3,4-dibromocyclohexane |  |

| Trade Name | Manufacturer/ Supplier[1] | Recommended Use[2] |
|---|---|---|
| FireMaster PHT4 | VEL | PES |
| Great Lakes DBP | GL | ABS, PMMA, PP, PS |
| Great Lakes T1-82 | GL | ABS, PS |
| - - | DOW<br>ET | AC, PVAC, PVC |
| CITEX BCL-462 | CS | CA, PP, PS, PUR, PVC |

## Table 1b. Bromine Based Fire Retardant
(Unknown structures)

| Fire Retardant | Composition (%) | Trade Name | Manufacturer/ Supplier$^{(1)}$ | Recommended Use$^{(2}$ |
|---|---|---|---|---|
| Brominated Organic Comp. | Br-29; Cl-40 | CITEX BC-26 | CS | ABS, AC, CA, PE, PP<br>PS, PUR, PVAC |
|  | Br-47 | CITEX BN-451 | CS | CA, CN, EP, PA, PES<br>PP |
|  | Br-40 | CITEX BN-21 | CS | AC, CA, EP, PA, PE,<br>PP |
|  | Br-67 | CITEX BT-93 | CS | CN, EP, N, PC, PE,<br>PES, PP, PS, PUR,<br>PVAC, PVC |
|  |  | CAVGARD FR-1546 | GL | PVAC |
|  | Br-63, Cl-21 | HFO 103 | HEX | ABS, PES, PUR |
|  | Br-67 | HFO 104 | HEX | ABS, PES, PUR |
|  |  | FireMaster RBF-1 | MIC | PUR |

| Fire Retardant | Composition (%) | Trade Name | Manufacturer/ Supplier(1) | Recommended Use(2) |
|---|---|---|---|---|
| Phosphonium bromide | Br-13.2;P-20.3;N-13.8 | CYAGARD RF-473 | AC | ABS, PE, PO, PP, PS |
| Polyol | Br-35;P-2.6 | Brominex 160P | GL | PUR |
|  | Br-23;P-2.6 | Brominex 161P | GL | PUR |
|  | Br-26;P-4.0 | Brominex 163P | GL | PUR |
|  | Br-48;P-1.9 | Brominex 214P | GL | PUR |
|  | Br-73 | Brominex 257 | GL | PUR |
|  | Br-41;P-2.7 | Brominex 711P | GL | PUR |

(1) Manufacturers/Suppliers

AC - American Cyanamid Co., Polymers and Chemicals Dept.,
Bound Brook, N. J., 08805

CS - Cities Service Co., Flame Retardants Dept.,
Drawer 4, Cranbury, N. J., 08512

DOW - Dow Chemical Corp.,
2020 Dow Center, Midland, Mic, 48640

ET - Ethyl Corp., Industrial Chemicals Div.,
Ethyl Tower, 451 Florida, Baton Rouge, La., 70801

GAF - GAF Corp.,
140 W. 51 Street, New York, N.Y., 10020

GL - Great Lakes Chemical Corp.,
P.O. Box 2200, W. Lafayette, Ind., 47806

HEX - Hexcel Corp., Fine Organics Div.,
205 Main Street, Lodi, N. J., 07644

MIC - Michigan Chemical Corp.,

ST - Stauffer Chemical Co., Specialty Chemicals Div.,
Westport, Conn., 06880

VEL - Velsicol Chemical Corp.,
341 East Ohio Street, Chicago, Il., 60611

KE - Keil Chemical Div., Ferro Corp.,
3000 Sheffield Avenue, Hammond, Ind., 4632

PEA - Pearsall Chemical Co.,
P.O. Box 437, Houston, Tx., 77001

## (2) Polymers

ABS - Acrylonitril - Butadiene - Styrene

AC - Acrylis

CA - Cellulose acetate

CN - Cellulose nitrate

EP - Epoxy

PA - Polyamide

PAN - Polyacrylonitril

PC - Polycarbonate

PE - Polyethylene

PES - Polyester

PETH - Polyether

PH - Phenolic

PMMA - Polymethylmethacrylate

PO - Polyolefin

PP - Polypropylene

PS - Polystyrene

PVAC - Polyvinylacetate

PUR - Polyurethane

PVC - Polyvinyl chloride

R - Rubber

# APPENDIX D

## Carcinogenic Risk Assessment from Airborne Exposure to Ethylene Dibromide

# Carcinogenic Risk Assessment from Airborne Exposure to Ethylene Dibromide

To estimate the risk of contracting cancer from ethylene dibromide, two factors must be known: the exposure and the risk factor. The exposure was estimated by Mara and Lee (1978), the results, along with some manipulations by Winzler and Kelly, being presented in Table 2.2-3. The total exposures for c. 1975, 1980 and 2000 are $490 \times 10^6$, $360 \times 10^6$, and $170 \times 16^6$ person-ppt, respectively, which are equivalent to 3.7, 2.8, and 1.3 person-mg/l, respectively ($1.30 \times 10^8$ ppt EDB = 1 mg/l; see Table 2.2-1). At an average respiratory volume of $2.0 \times 10^4$ l/d (see Table D-1), the exposures are transformed again to $7.4 \times 10^4$, $5.6 \times 10^4$, and $2.6 \times 10^4$ person-mg/d (e.g., $3.7 \times 2.0 \times 10^4 = 7.4 \times 10^4$).

EPA estimated occupational exposures and carcinogenic risk associated with pesticidal applications of EDB (Table 2.2-4). We calculated the average of the carcinogenic risk factors in Table 2.2-4 -- 0.016 cancer/person-yr per mg/kg-d -- assuming a lifetime of 71.3 yr (U.S. EPA, 1980). Assuming an average weight of all individuals in the U.S. of 60 kg (132 lb), which we estimated from data contained in the Statistical Abstract of the U.S. (U.S. Bur. Census, 1979), we transformed this risk factor to $2.7 \times 10^{-4}$ cancer/person-yr per mg/d (0.016/60).

Taking the product of the exposures ($7.4 \times 10^4$, $5.6 \times 10^4$, and $2.6 \times 10^4$ person-mg/l) and the risk factor ($2.7 \times 10^{-4}$) yields the estimated cancer incidences for c. 1975, 1980, and 2000 -- 20, 15, and 7 cancers per year, respectively -- from non-occupational atmospheric EDB exposures in the U.S., based on population exposure estimates of Mara and Lee (1978) and carcinogenic risk probability estimates of EPA (U.S. EPA, 1980). From Table 2.2-3, we see that nearly 80% of the cancer incidence would be attributable to persons living in vicinity of gasoline service stations.

Because of the uncertainties involved in this estimation, the major ones being the carcinogenic potency of EDB in humans (which could be zero) and the population exposure estimates, the computed cancer incidences could be off by up to several orders of magnitude.

Table D-1. Estimation of Average Respiratory Volume

| | Respiratory Volume (l/d)[a] | Population[b] |
|---|---|---|
| Men | $2.3 \times 10^4$ | $82.2 \times 10^6$ (14 yrs. +) |
| Women | $2.1 \times 10^4$ | $81.0 \times 10^6$ (14 yrs. +) |
| Children | $1.5 \times 10^4$ (10 yrs.) | $31.4 \times 10^6$ (5 to 13 yrs.) |
| Infants | $0.38 \times 10^4$ (1 yr.) | $15.4 \times 10^6$ (under 5 yrs.) |
| | | $210 \times 10^6$ |
| Weighted-Average | $2.0 \times 10^4$[c] | |

[a] Source: NAS, 1978, p. 165

[b] Source: U.S. Bur. Census, 1979, p. 29

[c] $(2.3 \times 82.2 + 2.1 \times 81.0 + 1.5 \times 31.4 + 0.38 \times 15.4)\ 10^4/210 = 2.0 \times 10^4$